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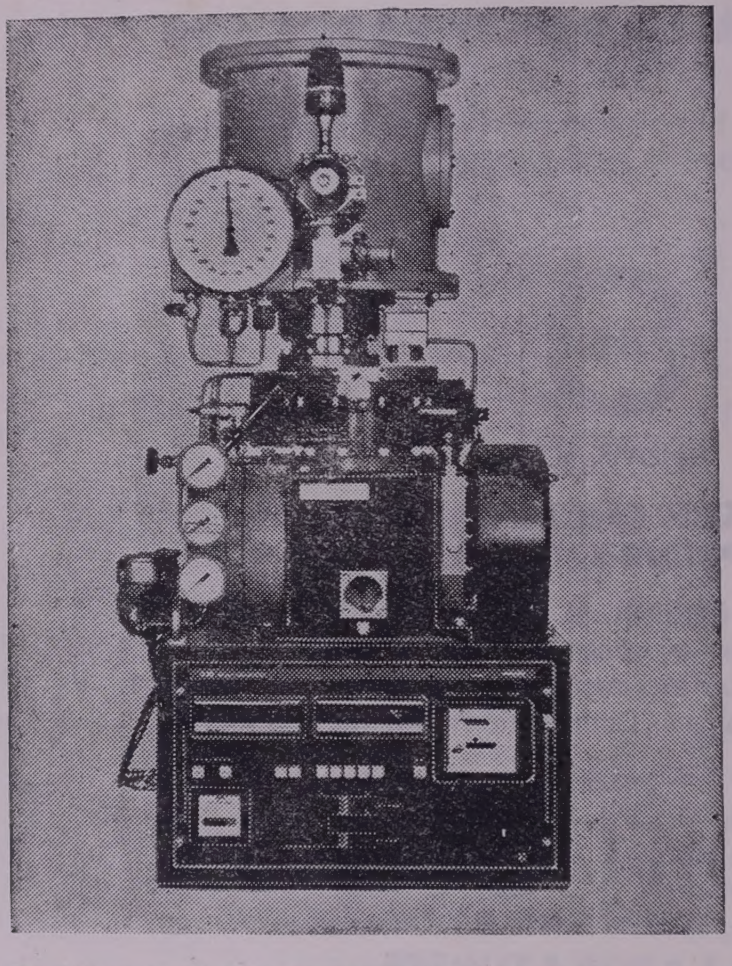

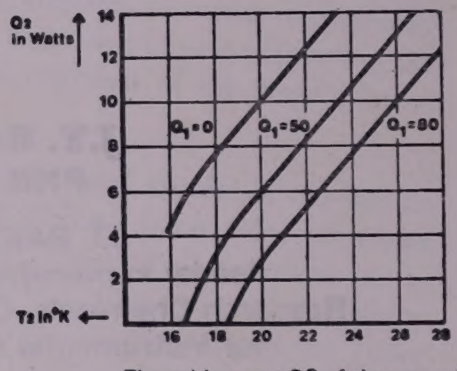

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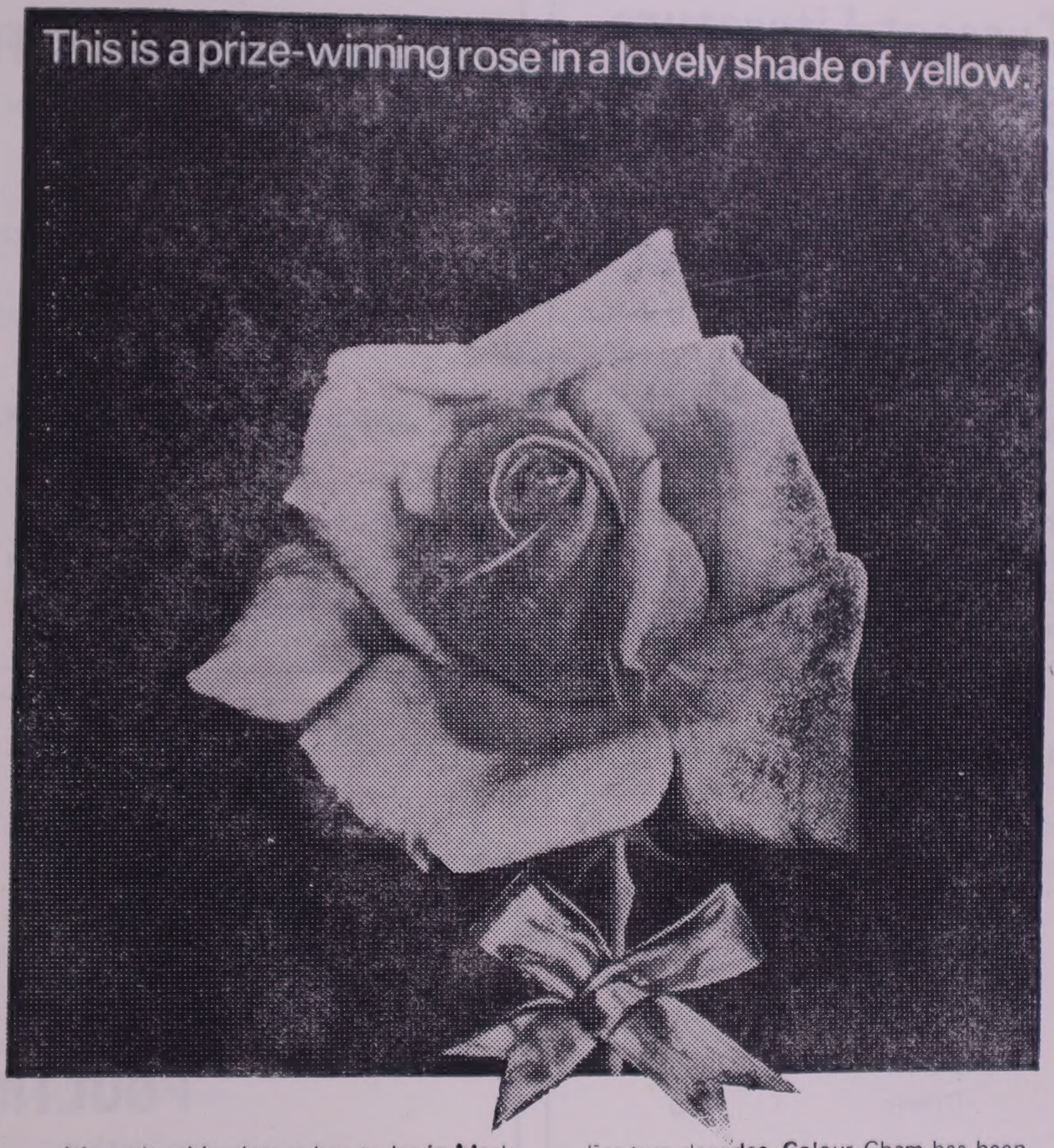

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Clinical Genetics in India—Present Status

ARCHANA SHARMA
Chromosome Research Centre, Department of Botany, University of Calcutta, Calcutta 700 019

In India, the incidence of diseases due to environmental factors, including nutritional and infectious ones, earlier tended to obscure the anomalies due to genetic causes. The control of smallpox and related viruses and the prevention of diseases like cholera and malaria are gradually uncovering the extent of genetic disorders present. As yet, our knowledge regarding such abnormalities is at the stage of accumulation of data and has not yet reached the stage where analysis and interpretation could be attempted.

The simplest method of classifying genetic and chromosomal defects surviving as defective individuals in nature is to divide them into those of monogenic and polygenic inheritance. The former can further be subdivided into those of autosomal dominance, autosomal recessive and sex chromosomal inheritance. The polygenic control may be exerted directly on the character or may be modified by gene-environment interaction. The disorders due to chroosomal changes form a separate category. They may be structural or numerical, involving sex chromosomes or autosomes.

Actually, in India, most of the human genetic disorders were recorded as congenital defects, without any initial knowledge of their genetic causes. Data on genetic disorders have originated mainly as case reports or from surveys of small subpopulations, like tribals, for anthropological parameters. No systematic survey has yet been undertaken of the different populations of the country, taking into account the variations in ethnic groups and environmental factors.

Congenital Defects

These defects account for 0·68% of neonatal deaths in India (*Vital Statistics*, Govt. of India, 1972). They include, in addition, mental deficiency, spina bifida, cleft lip and palate. Many such disorders have been established as being due to polygenic inheritance, while others may be environmental or due to gene-environment interaction. The estimates, as given by different workers in different areas, vary for different forms. A total estimate of congenital anomalies of all systems gives figures varying from 3·1 to 20·36 per 1000 live births (WHO 1966). Sporadic records are available without attempts at population study of defects like multiple skeletal syndromes and alimentary tract obstructions. The final incidence of such defects in populations or their distribution in any particular area is not known. Most of them show autosomal dominance and occur as isolated cases.

The most exhaustive data on genetic anomalies available in India are those on haemoglobinopathies. They include both case reports and population studies, using techniques ranging from chemical to electrophoretic ones. The records from selected small isolates give conclusive evidence for inheritance. Those from city hospitals are, however, less definite due to the heterogeneous nature of the samples. Most of the major haemoglobins, S, D and E, have been reported in various subpopulations, while Hb H, J, K, L, M, Q and Hb Lepore, Barts and Norfolk are of rarer occurrence.

Sickle cell anaemia and sickling trait occur in significant frequencies in aboriginal tribals in different parts of India, except northwest and extreme south. Reports from other areas are scattered ones. No definite relationship with external factors has been established.

HbE trait shows a wide distribution over India, in frequent association with β-thalassaemia and HbEE, though the reports from eastern India and Bombay are more frequent. It is highest in certain regions of Assam and has been suggested as a marker for the mongoloid element in the northeast Indian populations. β-Thalassaemia major has been diagnosed in nearly all states of western India as well. There is an interaction between HbβT and HbβE, leading to greater anomalies in such individuals than in HbT-normal heterozygotes and HbEE homozygotes.

HbD shows a tendency to cluster in populations originating from northwest India, like Sikhs, Punjabis, and Sindhis and their descendents settled in other parts of India. Isolated reports may possibly be attributed to mutations.

Other haemoglobin variants include Hb Punjab, HbK, M, L and Q, reported from different parts of India. Screening of the armed forces gave an overall incidence of 0·96% abnormal Hb. A recent report on Gorkhas from Nepal shows an overall incidence of 1·33% abnormal Hb, including HbAE, HbA Norfolk and HbAJ. Other reports are mainly sporadic ones.

α-Thalassaemia, Hb Barts, HbH and Hb Lepore have been observed during surveys made in Bombay and Calcutta, the last one having been recorded once only.

Thalassaemias, in association with variant haemoglobins, like HbS and D, have been observed, though in relatively low frequencies. Blood coagulation defects have been identified in a few families.

The major difficulty in the identification of other diseases of recessive inheritance is the dependence on clinical criteria, many of which resemble those due to non-genetic causes.

Lipid storage diseases have been reported from different regions. The diagnosis is usually delayed due to the fact that hepatosplenomegaly—its principal criterion—is also caused by several tropical diseases like malaria and leishmaniasis. Glycogen storage diseases have been reported but in low frequencies. Gaucher's disease is usually diagnosed through liver biopsy and enzyme studies are not carried out in most hospitals.

Mucopolysaccharoidoses are sufficiently well marked clinically to be identified relatively easily. Sporadic case reports appear from many centres.

Indian childhood cirrhosis has not been yet fully analysed regarding its inheritance pattern and causation, though it is of quite frequent occurrence. In most neonatal surveys in large cities, a significant number of cases of hyperbilirubinaemia has been ascribed to G6PDase deficiency.

G6PDase deficiency exists in adult populations nearly all over India in frequencies varying from less than 1 to 15·8% and in high frequencies in Sri Lanka. Malarial endemicity was regarded as a causative factor and thalassaemia was found to be associated in some cases with this deficiency.

Data on aminoacidurias are meagre. Individual reports are available of phenylketonuria, homocystinuria, alkaptonuria and maple syrup urine disease in different zones. Porphyria, including the acute intermittent type has been recorded from various parts.

Muscular dystrophies are fairly common in India, but details regarding their incidence are not yet available. The same is true of inherited coagulation diseases, including haemophilia and various disorders of the skin. The low incidence of such disorders may also be attributed to lack of diagnosis. A large number of inherited diseases may escape detection due to masking by other environmental factors, including the unsatisfactory nutritional status. For example, vitamin D resistant rickets has been recorded in Asian immigrants to western countries. It could be related to the rickets commonly prevalent in north India.

Alterations of the Human Chromosome Complement

Alterations involving deletion, duplication or translocations of small segments and addition of the short acrocentrics, have been associated with certain well-known syndromes. The recent advent of differential banding patterns has enabled the identification of several new syndromes. In India as yet, the records on chromosomal aberrations are mainly based on the earlier air drying-Giemsa staining schedule and banding patterns have not been used extensively in diagnosis.

The few surveys of newborns are from urban hospitals and, therefore, do not give a correct picture. The occurrence of chromosomal abnormalities, including both sex chromosomal and autosomal anomalies, has been estimated at 3-4 per 1000 live births. However, rural populations have not been covered.

Sex chromosomal abnormalities are the most common ones. Mosaics, gonadal dysgenesis and Mullerian duct aplasia are frequent among the cases investigated at gynaecological outpatient departments.

Of the autosomal disorders, Down's syndrome has been recorded most frequently. Majority of them carry a translocation for chromosome 21, though trisomy 21 has also been diagnosed in several cases. Maternal age does not seem to have a significant influence. Association with certain environmental factors has been observed in certain cases, as for example, an apparent increase in cases of Down's syndrome born to women living in areas of high background radiation in Kerala. Observations from a Calcutta hospital show the highest frequency of Down's syndrome births in December/January, giving the period of conception as April/May—the driest and hottest season of the year, with low nutrition and high viral infections.

The problems faced in assessing diseases due to genetic causes in India are manifold, partly due to the number and partly also to the multiracial nature of its peoples and the multienvironmental nature of the country. Most data are in the form of case reports or assays from small adhoc groups. A primary difficulty is the absence of adequate records of births, marriages and deaths, particularly in the rural areas. Since 80% of births occur in villages, the surveys made on the relatively heterogeneous urban populations present an incomplete, and often, erroneous picture. Lack of adequate and simple screening techniques for screening heterozygotes of most of the single gene deficiencies, forms a major lacuna. In addition, facilities for diagnosis requiring sophisticated techniques are available in only a few large institutions.

The accumulation of data, followed by their analysis, will require suitable screening programmes in collaboration with population geneticists. Carefully planned sampling techniques will be needed with a detailed understanding of historical, demographic and genealogical relationships of people living in different environments. The basic criterion for screening for any error of metabolism would be previous reports of its incidence in the population to be screened.

Undergraduate medical teaching should include clinical genetics—its general principles, methods of diagnosis and incidence in India—as an important part of the curriculum. General practitioners may be offered special or refresher courses in the subject, to enable them to diagnose whether a case is due to genetic or genetic-environmental causes and to send it to district hospitals. The latter may be provided with small genetic units, capable of identifying relatively simple anomalies and of referring more complex cases to city hospitals. The final diagnosis may be made in city referral hospitals having more sophisticated facilities. A preliminary survey should, however, be carried out of different regions to identify the types of diseases expected in a particular area due to the obvious impracticability of providing all city hospitals with facilities for diagnosing all possible disorders.

With the progressive unmasking of diseases of genetic origin following the decrease in those due to infection and malnutrition the need for genetic counselling is gaining recognition. Since prevention is of primary importance in such cases, the need for genetic counselling for both parents and practitioners has to be stressed. The future development of medical genetics thus, has prospects in both genetic counselling in the well-being of a healthy family and in solving problems of fundamental interest.

Guidelines Proposed in the Assessment and Containment of Genetic Disorders

In the Indian context the detection of abnormal genotypes may be carried out at three levels.

(a) Primary screening through routine diagnosis at primary health centres, family welfare units and dispensaries at the village level may be visualized through reports of congenital malformations and repeated still births, followed by simple urine or blood tests, wherever possible.
(b) Tentative cases may be sent to eth district hospitals which will have facilities for sex chromatin analysis and routine biochemical tests for more common disorders with collection of pedigree data.
(c) The final diagnosis will be carried out at city hospitals with genetic counselling units and having provision for chromosome analysis, specialized tests for biochemical disorders, genetic counselling and the maintenance of a genetic register.

Population screening for genetic disorders — In India this should form a separate drive with simple tests and/or enquiries for preliminary identification. It may be attached to the birth registration centres or the census teams or survey teams of the Anthropological Survey or vaccination drive centres. The visualization of population screening as a separate survey is definitely advantageous but, hardly feasible from the economic standpoint.

Family screening — This is relatively simpler, for individual disorders, once they have been diagnosed, both in district and city hospitals. It can be recommended after the detection of an affected individual in cases of high risk, mainly for diseases with a complex inheritance. Risk registers can be maintained for genetic counselling but only at city reference hospitals in the first phase. The same method may be applied for screening small groups at risk, as for example, inbred tribals in Korapur area for HbS.

Parental screening — This is required in families of established diseases before planning the next child. This is possible only in cases where complete family history with diagnosis of the condition is available.

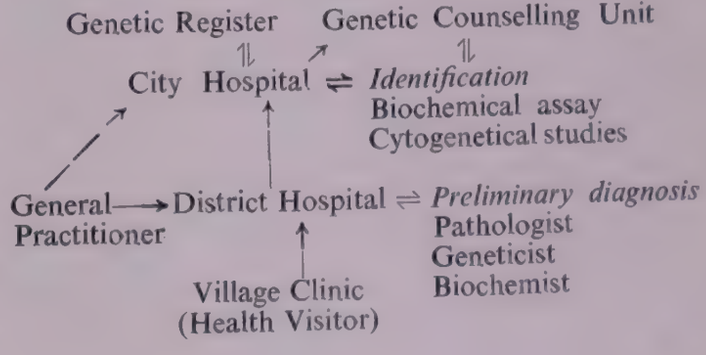
In introducing genetic counselling and diagnosis of hereditary diseases, education should be provided at different levels, both to promote consciousness of such diseases and knowledge about their diagnosis and mode of inheritance.

At the specialist level, such education may take the form of a postgraduate diploma or a doctorate degree in medical genetics for both medical and science graduates with the requisite background. These personnel would man the city genetic clinics and referral hospitals. In district hospitals, the technicians may be medicine, biochemistry and biology graduates with 3-6 months' training in medical genetics. Refresher courses of the same duration are required for general practitioners as well. The health visitors, or social workers in the units at the village level, should be given basic training which would equip them with basic knowledge of the principles of genetic disorders, of preliminary pathological tests for their identification and of the information to be collected in such cases.

At the initial stage, the public needs education in the incidence of such afflictions and the necessity of their diagnosis and prevention, by audiovisual means through different mass media and the curricula of basic and applied genetics at school and college levels require orientation in this direction.

The following are the major lines for future research.

(i) Fundamental research aimed at identification and assessment of the occurrence of individual diseases, their characteristics and possibilities of prevention and palliation.
(ii) Maintenance of a genetic register involving follow-up studies of individual disorders, effects on the gene pool, appraisal of the system, assessment of prevalence and the arousal of public consciousness. The register for abnormalities may be prepared on the basis of geographical, political or climatic considerations.
(iii) Application to Indian conditions, requiring (a) improvements in methodology for general use, with special emphasis on indigenous products; (b) maintenance of registers at progressive smaller units, and (c) prevention compatible with local conditions.



Particle-Fluid Heat Transfer in Fixed and Fluidized Beds

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PARTICLE-FLUID heat or mass transfer is of prime importance in a number of industrial processes. These operations may range from simple heat recovery as in the case of gas cooled granular catalyst beds or pebble bed heaters to complex systems involving simultaneous heat and mass transfer with or without chemical reaction. In all these processes the particles are usually in the form of a bed, either fixed or fluidized, through which a fluid flows. To design adequate and effective industrial equipment for these processes, it is necessary to work out a method of engineering calculation for heat and mass transfer between fluid and particles. This requires a sound knowledge of the rate of heat or mass exchange between solid particles and fluid and the associated pressure drop through the bed. Vast amount of published information exists in the literature on these three subjects. The present communication summarizes and assesses the information concerning particle-fluid heat transfer.

In summarizing the reported studies an attempt has been made to include as far as possible all the published investigations on fluid-particle heat transfer; however, many references might have been left out because of difficulty in having access to the original source. All the pertinent references (1-349) cited are arranged in chronological order to facilitate their easy location. The available information is summarized in Table 1 and Figs 1-3. The general trend of particle-fluid heat transfer under various situations is also shown in Fig. 4. Attention has been confined only to particle-fluid heat transfer and for information concerning other modes of heat and mass transfer and pressure drop, reference should be made to other sources (ref. 42, 70, 91, 261, 263, 309, 334, 350). From time to time, many other workers have also tried to summarize the then available information on particle-fluid heat transfer (ref. 47, 65, 68, 70, 91, 136, 180, 181, 263, 309, 334, 345). Except for the work of Barker (ref. 180, 181), the information available from most of these sources are rather limited in scope. An attempt has been made to overcome this limitation by including as much information as possible in the present review.

From the survey of the literature, it is clear that particle-fluid heat transfer in both packed and fluidized beds has been measured by using either steady state techniques (ref. 10-15, 22, 24-29, 32-34, 37, 40, 42, 46, 48-51, 54, 57, 58, 64, 71-74, 77, 80, 84, 86, 87, 89, 90, 92-95, 97-103, 105, 107, 108, 112, 116, 119, 123, 124, 126-129, 131, 132, 134, 141-143, 145, 146, 148-151, 155-159, 169-173, 176, 177, 179, 183-185, 189, 191, 192, 194, 196, 198-200, 202, 203, 207-211, 215, 216, 218-225, 227-233, 235, 237, 242, 243, 245-247, 250-257, 259-262, 264, 266-270, 274, 278-283, 287-289, 292-294, 296, 297, 300, 302-304, 306, 308, 312-315, 317-321, 323, 326-331, 337, 340, 342-344, 346-349) or unsteady state techniques (ref. 1-9, 11, 16-21, 23, 29, 30, 34-36, 38, 39, 41, 43-45, 52, 53, 55, 56, 59-63, 66, 67, 69, 75, 76, 81-83, 85, 86, 88, 96, 104, 109-111, 117-122, 125, 130, 133, 135, 137-140 144, 147, 152-154, 160-168, 177, 178, 182, 186-188, 192, 193, 195, 197, 201, 204-206, 212-218, 223-226, 230-234, 238-241, 244, 246, 248 249, 258, 265-267, 271-273, 275-277, 281, 284-286, 289-291, 294-296, 298-301, 305, 307, 310-312, 316, 322, 324-326, 332, 333, 335, 336, 338, 339, 341). In the steady state techniques, rate data have been obtained either by estimating the heat changes accompanying evaporation of a liquid from the surface of porous particles forming the bed or by using induction heating or direct electrical heating of the bed. In the unsteady state techniques, temperature-time history graphs have been used to evaluate the heat transfer rate. In some cases, frequency response technique or heat changes accompanying a suitable chemical reaction have also been used.

Fixed bed measurements (ref. 3, 9-22, 26, 30, 31, 34, 35, 37, 40-43, 53-55, 58, 59, 79, 80, 83, 93, 98, 101-103, 106, 114, 122, 126, 128, 131-134, 141, 146, 152, 173, 188, 191, 200, 210, 262, 272, 278, 297, 299, 301, 316, 324, 328) have been made for beds of spheres oriented in a regular pattern, such as cubic, hexagonal, rhombohedral, etc. and for randomly packed beds of spheres, cylinders, granules and commercial packings. Many workers have used distended packed beds in their measurements. In some cases, the beds have been diluted with inert spheres and many investigators have used single active spheres forming a part of the packed bed.

Fluidized bed measurements (ref. 24, 25, 27, 31-33, 35, 36, 38, 42, 45, 46, 52, 56, 57, 62, 66, 72, 73, 77, 81, 82, 86-88, 90, 97, 103, 104, 107, 110, 116, 124, 126, 132, 137, 142, 148, 153, 158, 168, 175, 179, 189, 191, 206, 213, 217, 238, 251, 253, 256, 272, 286, 303, 304, 328) have been made mostly with granules. Shallow beds have been used in most of the cases. Most of the measurements are again confined to air, although H_2, Ar and CO_2 have been used occasionally. In the case of liquid fluidized beds only water has been used as the fluid and that too only in two or three cases. Because of the use of small particles, the measurements are confined mainly to $Re < 100$ and no information is available for $Re > 100$.

Experimental measurements have been made mostly with gases and water. In the case of measurements with gases, air has been widely used as the test fluid (ref. 3, 9, 13-15, 17, 19, 21, 22, 24-27, 30-36, 38, 40, 41, 43, 45, 46, 52-56, 58, 59, 62, 66, 72, 73, 79-82, 85, 86, 94, 97, 98, 102, 104, 107, 110, 114, 116, 122,

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TABLE 1 — SUMMARY OF THE LITERATURE ON HEAT TRANSFER IN FIXED AND FLUIDIZED BEDS

Author(s)	Experimental technique	Fluid	Particle			Bed characteristics			*Re*	*Pr*	Correlation
			Material and shape	Size cm	Temp. °C	Nature and cross-section cm	Height cm	Void fraction (ε)			
Furnas[3]	*T*, step input of gas	Air, $P=1$, $T=38$–704	Iron, spheres	1·854–4·851	38–704	Packed 15·24	104·14	0·395–0·506	120–1200	~0·7	$h=0{\cdot}000144G^{0{\cdot}75}\times T\times 10^{1{\cdot}68\varepsilon-3{\cdot}56\varepsilon^2}$
Saunders and Ford[9]	*T*, hot and cold air in steps, outlet temp. followed	Air, $P=1$, $T=58\pm 24$	Steel, lead, glass, spheres	0·1587–0·635	58 ± 24	Packed 5·08–20·32	6·35–25·4	—	54–434	~0·71	$St\approx 0{\cdot}188$
Fedorov[10]	Constant rate drying	Air, $P=1$ $T=?$	Moscow coal grains	0·3–1·2	—	Packed	(2–10) $\times D_p$	0·51–0·575	20–1850	~0·6	$Nu=0{\cdot}23\ Re^{0{\cdot}863}$
Kitayev[11]	Correlations of Furnas[3] data	—	Iron, iron ore, coke; sphere, granules	1·85–4·86; 0·4–7·0	425–625; 125–1125	Packed ,,	—	0·395–0·506; 0·485–0·585; 0·512 0·53	67–1050; 92–4830; 92–4830	—	$Nu=0{\cdot}14\ Re^{0{\cdot}92}$ $Nu=0{\cdot}098\ Re^{0{\cdot}9}$; $Nu=0{\cdot}104\ Re^{0{\cdot}9}$; $Nu=0{\cdot}06\ [A/(1-\varepsilon)]\ Re^{0{\cdot}9}$ where $A=10\ (1.68\ \varepsilon-3{\cdot}56\varepsilon^2)$
Sokol'skii[12]	Heat transfer during combustion of grains (a theoretical study)	Air, $P=1$ $T=?$	granules	—	—	Packed	—	—	—	~0·6	$Nu=2+a\ Re^{0{\cdot}5}$ For Re <100 $Nu=0{\cdot}56\ Re^{0{\cdot}5}$ For $Re\geqslant 100$
Gamson *et al.*[13]	*S*, constant rate drying	Air, $P=1$, $T=27$–54	Celite, spheres, cylinders	0·3962–2·162	15–52	Packed 30·48 × 30·48	2·54–6·35	0·37–0·43	60–4000	0·72–0·75	$J_h=18{\cdot}1/Re$, For $Re<40$ $J_h=1{\cdot}064\ Re^{-0{\cdot}41}$ For $Re>350$
Hurt[14]	*S*, constant rate drying	Air, $P=1$, $T=13$–27	Celite cylinder	0·953	—	Packed 8·382	5·08	-	72–840	0·83	$H_T\ Pr^{-2/3}=f\ (Re)$

(Contd)

TABLE 1 — SUMMARY OF THE LITERATURE ON HEAT TRANSFER IN FIXED AND FLUIDIZED BEDS (*Contd*)

Aurthos (s)	Experimental technique	Fluid	Particle			Bed characteristics			*Re*	*Pr*	Correlation
			Material and shape	Size cm	Temp. °C	Nature and cross-section cm	Height cm	Void fraction			
Wilke and Hough[15]	*S*, constant rate drying	Air, $P=1$, $T=27$–54	Celite cylinders	0·3962–2·162	15–52	Packed 30·48 × 30·48	2·3368	—	40–350	~0·7	$J_h=1{\cdot}95\ Re^{-0{\cdot}51}$
Chukhanov and Shapatina[16]	*T*, unsteady state heat transfer	—	Copper-cylinder; fireclay-granules	0·2 × 0·2; 0·2–0·7	—	Packed	—	0·4–0·52	—	—	$Nu=0{\cdot}24\ Re^{0{\cdot}83}$
Norton[17]	*S*, burning gases heat pebbles which in turn heat gases on moving down through the bed	Air, steam methane H_2, $P=1$, $T=38$–1040	Alumina-silica (72:28) spheres	0·7937–1·27	150–1150	Packed 48·26, 68·58	91·44–152·50	— —	157–619	~0·8	—
Chukhanov[18]	*T*, unsteady state heat transfer	—	Copper-cylinder; steel–sphere	0·2 × 0·2; 0·315	—	Packed	—	—	50–380	—	$Nu=0{\cdot}24\ Re^{0{\cdot}83}$
Glaser[19]	*T*, step input, reverse flow *S*, one sphere electrically heated	Air, $P=1$, $T=27$–94	Ceramic, brass-sphere	1·0, 1·94, 1·60, 5·207	—	Packed 35·05 —	96·52 —	0·392 0·42 — —	330–1500; 300–4000	~0·7	$Nu=1{\cdot}25\ Re^{0{\cdot}58}$
Kichkina[20]	*T*, unsteady heat transfer during drying	Air, $P=1$ $T=?$	Ceramic-granules	1·0–1·5	—	Packed	—	0·465–0·473	270–1350	—	$Nu=0{\cdot}229\ Re^{0{\cdot}815}$
Lof and Hawley[21]	*T*, Schumann curves	Air, $P=0{\cdot}82$ $T=38$–121	Granitic granules	0·7975–3·33	38–121	Packed 25·4 × 27·94	91·44	0·426–0·545	50–500	~0·7	$h'=0{\cdot}79\ (G/D_p)^{0{\cdot}7}$

Taecker and Houghen[22]	$\dot{S}$, constant rate drying	Air, $P=1$, $T=32$–42	Clay-kieselguhr								
			Raschig ring partition rings berl saddle	1·27–5·08; 5·08, 0·635–1·27	17–27	Packed 27·94	6·35–10·16	—	57–11000; 57–11000; 40–1700	—	$J_h=0\cdot91\ Re^{-0.41}$ For Raschig and partition ring $J_h=0\cdot759\ Re^{-0.34}$ For berl saddle
Timofeyev[23]	Empirical correlation of others data	Air, $P=1$, $T=?$	Steel, iron ore coal, gypsum-spheres, grains	—	—	Packed	—	—	—	—	$Nu=0\cdot106\ Re$, $20<Re<200$ $Nu=0\cdot61\ Re^{0.67}$, $Re\geqslant200$
Fedorov[24]	S, constant rate drying	Air, $P=1$, $T=40$–50	Active carbon, Moscow coal, card-board granules pieces	0·3–0·5 0·5–1·0 5×6×3–10×5×3 mm piece	—	Fluidized 10·0	0·6–4·5	—	G=0·9 4·0 kg/m² sec	~0·7	$Nu=0\cdot23\ Re^{0.863}$; $20<Re<500$ $Nu=0\cdot0151\ Fe^{0.74}\ Re^{0.65}\left(\frac{Ho}{de}\right)^{-0.34}$ for $30<Fe<100$ $Nu=0\cdot0283\ Fe^{0.604}\ Re^{0.65}\left(\frac{Ho}{de}\right)^{-0.34}$ for $100<Fe<200$
Kettenring *et al.*[25]	S, constant rate drying and humidification	Air, P=1, $T=17$–44	Alumina, silica gel granules	0·0502–0·0713	17–29	Fluidized 5·842	10·16–20·32	0·6–0·8	9–55	~0·72	$J_h=0\cdot0151\ Re^{0.30}$
Lydersen[26]	S, heated copper sphere in celluloid matrix	Air, $P=1$–5·6 $T=18$	Copper, celluloid spheres	3·785	24–60	Packed 7·57×7·57	22·71	0·2594–0·4764	120–4500	~0·71	$J_h=1\cdot187\ Re^{-0.37}$
Sato *et al.*[27]	S, heating of solids continuous feed and withdrawal	Air, $P=1$, $T=?$	—	0·016–0·064	29·4	Fluidized 18·0	—	—	3–40	0·7	$Nu=0\cdot03$–$1\cdot5$

(Contd)

TABLE 1 — SUMMARY OF THE LITERATURE ON HEAT TRANSFER IN FIXED AND FLUIDIZED BEDS (*Contd*)

Author(s)	Experimental technique	Fluid	Particle			Bed characteristics			*Re*	*Pr*	Correlations
			Material and shape	Size cm	Temp. °C	Nature and cross-section cm	Height cm	Void fraction			
Dayton *et al.*[29]	*T*, Frequency response	Air, $T=28$–48 $P=?$	Glass spheres	0·3275–0·6299	28–48	Packed	2·54–4·08	—	150–1000	~0·71	$J_h = Re^{-0.41}$
Eichhorn and White[30]	*S*, dielectric heating	Air, CO_2, $P=1$, $T=2$	Plastic	0·0102 0·0658, 0·014–0·0841	—	Packed fluidized	—	0·35–0·384	1–18, 0·7–28	0·665 0·71	—
Walton *et al.*[31]	*S*, heating of particles by hot gas	Air, $P=1$, $T=118$	Coal granules	0·036–0·071	43–54	Fluidized 10·16	25·4–71·12	—	10–32	0·689	$Nu=0·00285\ Re^{0.7}\ (D_p/D_t)^{-0.2}$ $h=0·00762\ G^{1.7}\ D_p^{0.5}$
Anton[32]	*S*, heating of solids continuous feed and withdrawal	Air, $P=1$, $T=62$ (in)–46·1 (out)	Sand granular	0·37	29·4(in), 48·3–51·7 (out)	Fluidized 15·24	15·24–27·94 (fixed) 17·78–33·02	0·384–0·39, 0·49–0·606	2·4–8·5	0·702	$Nu=0·15$–$0·47$ $h=0·037\ [Re/(1-\varepsilon)]^{0.997}$ $J_h=0·00302/(1-\varepsilon)$
Maeda and Kawazoe[33]	*T*, heating of solids	Air, $P=1$, $T=?$	Celite, clay broken solids, Raschig rings, berl saddles	0·285–2·5	—	Packed 5·2–15·4	—	—	—	~0·7	$Nu=4·9\ Re^{0.60}\ \varepsilon^{-2.2}\ (Dp/Dt)$; $Re>100$ $Nu=12·3\ Re^{0.4}\ \varepsilon^{-2.2}/(Dp/Dt)$; $Re<100$ (*Nu Re* based on tube diameter)
Peters *et al.*[34]	*T*, cooling of solids particles	Air, $P=1$, $T=15$	Sand granular	0·023	50–115	Packed Fluidized	—	—	G=6·5–8·2 cm/sec	~0·7	$h=1$–$1·5$ kcal/m^2 hr degree
Shakhova[35]	*T*, heating of solid particles	Air, $P=1$, $T=?$	Quartz sand granules	0·0268–0·0564	—	Fluidized 7·85	—	—	9·51–1138	~0·7	$Nu=0·680\times10^{-2}\ Re^{1.55}\ N^{-1}$

Satterfield & Resnick[36]	S, $H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$ reaction	H_2O_2 $P=1$, $T=38$–205	Metal sphere	0·508	205–482	Packed 5·08, 7·62	2·54, 1·524	0·38–0·438	15–161	~0·708	$J_h = 0{\cdot}992\ Re^{-0.34}$
Wamsley and Johnson[37]	T, heating of solid particle by hot gas	Air, CO_2 $P=1$, $T=46$, 48 (inlet)	Alumina, glass, Dowex–50 granules, spheres	0·0228–0·0913, 0·0137–0·0455, 0·046–0·076	23–28	Fluidized 5·93	—	0·4–0·47 (static)	1–40	0·7–0·76	$h = 1270\ (D_p \text{ in ft})^{1.27}$
Dyakonov and Semenov[39]	S, cooling of induction heated bed	Air, $P=1$, $T=15$–45	Steel sphere	0·792–1·172	—	Packed 9·5	197	—	40–620	~0·6	$Nu = 0{\cdot}128\ Re\ (D_c/D_p)^{0.257}$
Glaser[40]	T, step input, reverse flow	Air, $P=1$, $T=27$–100	Clay, celite granules raschig rings	0·8224-1·6764	—	Packed 38·05	96·52	0·519–0·677	140–2000	~0·7	$Nu = 0{\cdot}96\varepsilon^{0.75} Re^{0.61}$
Chu[41]	S, based on analogy with mass transfer	—	—	—	—	Packed Fiuidized	—	—	10–10000	—	$J_h = 1{\cdot}77\ (Re/1-\varepsilon)^{-0.44}$; $Re/1-\varepsilon > 30$ $J_h = 5{\cdot}7\ (Re/1-\varepsilon)^{-0.78}$; $Re/1-\varepsilon < 30$
Coppage and London[42]	T, step input	Air, $P=1$, $T=32$	Lead sphere	0·2077	21–32	Packed 7·582	1·6764–2·9464	0·39	25–550	~0·71	$S_t = 0{\cdot}566\ Re^{-0.31}$
Fritz[44]	T, heating of solid particle by step input of hot gas	Air, $P=1$, $T=49$–83	Silica alumina micro-spherical	0·006	⩽49–83	Fluidized 40·6	11·43–120·7	—	1·2–13	~0·7	$U = \dfrac{u}{116 + 52{\cdot}4\,(L/D_t) + \dfrac{1 - 0{\cdot}6\,(L+D_t)}{274 + 447\,(L/D_t) + 146\,(L/D_t)^2}}$
Heertjes and McKibbins[45]	S, constant rate drying	Air, $P=1$, $T=21$	Silica gel sphere	0·0299–0·1198	15·5	Fluidized 6·0	—	—	8·8–52·3	~0·708	$h = 1{\cdot}310\ Re^{0.76}$ $J_h = 95{\cdot}7\ (D_p/Re^{0.24})$
Galloway *et al.*[48]	S, constant rate drying (partial spheres at wall)	Air, $P=1$, $T=21$	Celite, alundum, kasline spheres	1·7094	<21	Random & ordered packed 11·43 × 11·43	13·68	0·2595–0·4764	300–1200	~0·718	$J_h = 0{\cdot}197\ Re^{-0.159}$

(*Contd*)

TABLE 1 — SUMMARY OF THE LITERATURE ON HEAT TRANSFER IN FIXED AND FLUIDIZED BEDS (*Contd*)

Author(s)	Experimental technique	Fluid	Particle			Bed characteristics			*Re*	*Pr*	Correlation
			Material and shape	Size cm	Temp. °C	Nature and cross-section cm	Height cm	Void fraction			
Shakhova and Rychkov[51]	*T*, step input of hot sand	Air, $P=1$, $T=?$	Quartz sand granular	0·0268–0·0564	—	Fluidized 7·874	<90	—	2–170	0·708	$Nu=0{\cdot}00353\ Re^{2{\cdot}1}\ (G/Gmf)$ $J_h=0{\cdot}00285\ Re^{1{\cdot}53}\ (G/Gmf)$
Ball[52]	*T*, Frequency response, sine wave gas inlet	Air, $P=1$, $T=60$–94	Lead, alumina spheres	0·4394, 0·419	60–94	Packed 14·61	12·7–63·5	0·355–0·402	68–116	0·73	$J_h=0{\cdot}913\ Re^{-0{\cdot}324}$
Baumeister and Bennett[53]	*S*, induction heating	Air, $P=1$ $T=32$–149	Steel spheres	0·3175–0·3967	43–154	Packed 10·16	10·16	0·354	200–10400	~0·73	$J_h=a\ Re^b$, a and b depend upon particle size
Dabora *et al.*[54]	*T*, regenerator, step	Air, H_2 $P=68$, $T=1038$, 705	Alumina pebbles	1·137	~1038 ⩾705	Packed 31·75, 4·445	335·3, 94	— —	225–3700	~0·689	$J_h=0{\cdot}136\ Re^{-0{\cdot}298}$; air $J_h=100\ Re^{-0{\cdot}41}$
Ferron[55]	*T*, heating of solid particles	Air, $P=1$, $T=?$	—	0·06	—	Fluidized 7·62–20·3	—	—	0·8–19	~0·7	$Nu=(0{\cdot}2\text{–}80)\times10^{-4}$
Frantz[56]	*S*, evaporation of brine solution	Combustion gas, $P=1$, $T=?$	—	0·0225	—	Fluidized 10·2	—	—	1·3–2·8	0·65	$Nu=0{\cdot}02\text{–}0{\cdot}06$
Glaser and Thodos[57]	*S*, electric resistance of bed used to generate heat	Air, CO_2, H_2 $P=1$, $T=21$–100	Monel, brasss-spheres, steel cubes, cylinders	0·4762–0·794, 0·635–0·9525	65·6	Packed 4·7625	5·08	0·436–0·453, 0·417, 0·469, 0·477, 0·478	30–3000, 45–2100, 30–2100	0·71, 0·665, 0·715	$J_h=0{\cdot}535/[1{\cdot}1872\ \{Re/(1-\varepsilon)\}^{0{\cdot}3}-1{\cdot}6]$, for spheres $J_h=0{\cdot}535/[1{\cdot}393\ \{Re/(1-\varepsilon)\}^{0{\cdot}3}-1{\cdot}6]$, for cubes $J_h=0{\cdot}535/[1{\cdot}311\ \{Re/(1-\varepsilon)\}^{0{\cdot}3}-1{\cdot}6]$, for cylinders

Kruglov and Skoblo[58]	*T*, heating of falling particles by hot gases	Air, $P=1$, $T=90$–115	Lead, iron, horn blende, porcelain, Al-silicate coke spheres pellets	0·09–0·36	—	Falling bed 3·2	—	—	90–1980	0·7	$Nu=0\cdot157\ m^{-0\cdot14}Re^{0\cdot63}$ $m=(V_{particles}/V_{heating\ zone})$ also different equations for different materials
Rozental[61]	*T*, humidification falling rate drying	Air, $P=1$, $T=178$–22·8 (in)	Gelatine cubes, cylinders, rings	0·8382–0·9906	11·7–15·5	Fluidized 7·62 deep settled	—	—	630–3200	~0·68	$Nu=0\cdot00064\ Re^{1\cdot48}$ or $J_h=0\cdot000719\ Re^{0\cdot48}$
Ciborowski and Roszak[65]	*T*, thermal regime transfer	Air, $P=1$, $T=?$	Sand granules	0·029–0·1	—	Fluidized 4·9	—	—	—	0·7	No clear relation between effective heat transfer coefficient and *G*
Richardson and Ayers[71]	Q.S, heating, of particles	Air, CO_2 $P=1$, in $T=67\cdot2$–60 (out)	glass, lead, petunia seeds spheres	0·011–0·067	30 (in) 50–67·2 (out)	Fluidized 5·08 × 10·16 (rectangular)	1·016 (static)	0·5–0·64	0·53–34·4	0·72–0·76	$Nu=0\cdot054\ (Re/\varepsilon)^{1\cdot28}$
Sharlovskaya[72]	Q.S, heating, of particles	Air, $P=1$, $T=?$	Porcelain, quartz sand marble spheres grains	0·21–0·89, 0·0835, 0·1434–0·301	—	Fluidized 10·0	—	—	30–2500	~0·7	$Nu=0\cdot015\ Re^{0\cdot805}\ Fe^{0\cdot53}\ (Ho\ D_p)^{-0\cdot45}$ for $Fe=27$–294
Blickle and Nemeth[76]	—	Gas, $P=1$, $T=?$	—	—	—	Fluidized	—	—	30–10000	~0·7	$J_h=5\cdot7\ (Re/1\text{-}\varepsilon)^{-0\cdot78}$ for $30 < Re/1-\varepsilon < 10^4$ $J_h=1\cdot77\ (Re/1-\varepsilon)^{-0\cdot44}$ for $(Re/1-\varepsilon)<30$
DcAcetis and Thodos[78]	*S*, constant rate drying	Air, $P=1$, $T=25$	Celite spheres	1·5875	12·2	Packed 9·3776	4·763–7·938	0·482	13–2136	~0·72	$J_h=1\cdot1/(Re^{0\cdot41}-1\cdot5)$
Von der Decken[79]	*S*, evaporation	Air, $P=1$, $T=?$	Naphthalene spheres	3·0	21-22	Packed 60	60	—	—	~2·5	$Nu=f(Re)$

(*Contd*)

TABLE 1 — SUMMARY OF THE LITERATURE ON HEAT TRANSFER IN FIXED AND FLUIDIZED BEDS (*Contd*)

Author(s)	Experimental technique	Fluid	Particle			Bed characteristics			*Re*	*Pr*	Correlation
		shape	Material and	Size cm	Temp. °C	Nature and cross-section cm	Height cm	Void fraction			
Donnadieu[80]	*T*, heating of solids	Air, $P=1$, $T=?$	Grainules	0·043	—	Fludized 20·07	43·43	0·39	6–25	0·72	$J_h=0{\cdot}0097\ Re^{1.3}$ $J_h=0{\cdot}0449\ Re^{0.637}$
Kazakova *et al.*[81]	*T*, cooling of particles	Air, $P=1$, $T=?$	Aluminium nitrate granules	—	—	Fluidized	—	—	—	~0·7	$h=C\ Re^m$; where C and m depend upon the height of the fluidized layer
Lancashire *et al.*[84]	*T*, regenerator uneven initial bed temperature	Air, $P=1$, $T=?$	Sphere	1·0541	1148	Packed 121·9	317·5	—	80–300	~0·6	$J_h=0{\cdot}40\ Re^{-0.437}$
Muchi *et al.*[85]	*S,T*, heating or cooling of solid particles	Air, $P=1$, $T=?$	—	—	—	Fluidized 7·0	—	—	—	~0·7	—
Ruckenstein and Teoreanu[86]	New model & correlations	$P=1$, $T=?$	—	—	—	Fluidized	—	—	—	—	$Nu=0{\cdot}426\ Re^{0.30}\ Ar^{0.17}\ Pr^{1/3}$; for $Re\ Ar^{-0.4} < 2{\cdot}15$ $Nu=0{\cdot}943\ Re^{-1.0}\ Ar^{0.69}\ Pr^{1/3}$; for $Re\ Ar^{-0.4} > 2{\cdot}15$
Sunkoori and Kaparthi[87]	*T*, heating of solid particles	Water $P=1$, $T=26{\cdot}1$–29·4	Quartz, granite granules	0·054–0·11	90·6–100	Fluidized 8·24	20·32–45·72	0·68–0·885	12–42	~5·93	$Nu=0{\cdot}00391\ Re^{2.1}$
Baldwin[91]	*S*, one sphere heated electrically	Water $P=2{\cdot}7$, $T=116$	Aluminium spheres	4·9212	116·5–118·2	Packed ordered 21·94 × 21·94	30·48	0·261, 0·478	3000–70000	~5·9	$J_h=0{\cdot}992\ Re^{-0.33}$, after 5th row $J_h=0{\cdot}940\ Re^{-0.3}$, after 3rd row
Bowers and Reintjes[92]	*S*, heating of particles	Steam, CO_2, N_2 $P=1$, $T=316$–482	Anthracite, coal briquettes	3·353	—	Packed & moving 30·48 × 30·48	—	—	$G=166$–404	~0·7	$J_h=A\ Re^{-0.41}$

Ciborowski and Mlodzinski[93]	*S*, drying of particles	Air, $P=1$, $T=?$	Hydrated salt granular	—	—	Fluidized	—	—	—	~0·6	$Nu=0·0236\ Re^{1·1}$
Frantz[96]	Based on others data	Air, $P=1$, $T=682$–932 in 132–349 out	Salt granules	0·0225	132–349	Fluidized 10·16	15·24–27·94	—	1·3–2·8	0·65	$Nu=0·02075\,Re^{0·2}$, true coeff.: Frantz's data $Nu=0·01337\ Re^{1·6}\ Pr^{0·67}$; for true heat transfer coeff. $Nu=0·016\ Re^{1·3}\,Pr^{0·67}$; for apparent heat transfer coeff.
Kunii and Smith[97]	*S*, axial temperature profile	Air, $P=1$, $T=?$	Sand granules glass beads	0·024–0·102	—	Packed	—	—	0·02–0·9	0·71	—
Takeoka and Nagasako[100]	—	Air, $P=1$ $T=?$	Steel spheres	—	—	Packed (soldered)	—	—	—	~0·7	$Nu=1·26\ (Re/1-\varepsilon)^{0·576}\ (D_p\ D_t)^{-0·28}$
Wadsworth[101]	*S*, one sphere heated electrically	Air, $P=1$ $T=?$	Copper spheres	10·16	—	Packed ordered 30·48 × 30·48	50·8	0·2595	8000–60000	0·71	$J_h=St\approx 0·972\ Re^{-0·267}$
Yeh[102]	*S*, correlations based on others data	$P=1$ $T=?$	Sphere, raschig rings, berl saddles	—	—	Packed and fluidized	—	—	0·2–5000	—	$Nu=1·91\times 10^{0·04}\ Re\ Pr^{1/3}$; $10>Re$ $Nu=0·8\ Re^{0·65}\ Pr^{1/3}$; $Re>50$
Yoshida[103]	*T*, heating of solids	Air, $P=1$ $T=?$	—	0·016–0·11	—	Fluidized 11·1	—	—	4–100	0·7	$Nu=0·002$–$0·30$
Beek[105]	Correlation based on others data	—	—	—	—	Packed (all)	—	—	10–4000	—	$Nu=3·22\ Re^{1/3}\ Pr^{1/3}+0·117\ Re^{0·8}\ P_r^{0·4}$
Curievici and Peretz[106]	*S*, constant rate drying	Air, $P=1$ $T=?$	Ammonium nitrate granules	0·015–0·03	—	Fluidized 7·0	5–15	—	—	0·6	—

(*Contd*)

TABLE 1 — SUMMARY OF THE LITERATURE ON HEAT TRANSFER IN FIXED AND FLUIDIZED BEDS (*Contd*)

Aurthor (s)	Experimental technique	Fluid	Particle			Bed characteristics			*Re*	*Pr*	Correlation
			Material and shape	Size cm	Temp. °C	Nature and cross-section cm	Height cm	Void fraction			
Ferron and Watson[109]	*T*, heating and cooling	Humid air, $P=1$, $T=49$–$65{\cdot}6$, (heating) $T=26{\cdot}7$–$37{\cdot}8$ (cooling)	Silica-alumina catalyst granular	0·006	21·1–32·2 (heating) 54·4 (cooling)	Fluidized 7·62, 20·32	2·286–60·96	0·651 (settled)	$u=0{\cdot}08$–1·94 ft/sec	0·702	$h=0{\cdot}0029\ u^{0.5}\ D^{0.7}\ (L/D)^{-0.7}$ (British units)
Glaser[113]	*S*, electrical heating, heating and cooling of air	Air, $P=1$ $T=?$	Ceramic spheres	1·03, 1·21, 1·6, 5·2	—	Packed 35·0	96·0	0·392, 0·42	300–4000	~0·7	$Nu=1{\cdot}40\ Re^{0.58}\ Pr^{1/3}$
Heertjes[115]	*S*, Humidification, constant rate drying	Air, $P=1$, $T=25$	Silica gel spherical	0·0457–0·0939	<25	Fluidized 1·905–5·842	—	0·66–0·95	6–70	~0·6	$J_h=10\ \varepsilon_o^3\ (D_p/D_t)^{0.17}\ /\ (Fr')^{0.49}\ (Re')^{0.03}$ $19\ Fr' = V^2/\varepsilon^2 g D_p < 225$ $Re' = D_p V \rho_f/\mu_f\ \varepsilon_o$
Meek[121]	*T*, frequency response	Air, $P=1$, $T=22{\cdot}2$–$42{\cdot}2$	Steel spheres	1·0007	22·2–42·2	Packed 5·08 × 5·08; 15·24 × 15·24; 10·16	7·62, 11·94, 12·7, 12·7,	0·337, 0·364, 0·370, 0·395	900–4000	~0·7	$St=1{\cdot}92\ Re^{-0.38}$; $\varepsilon = 0{\cdot}34$ $St=2{\cdot}05\ Re^{-0.42}$; $\varepsilon = 0{\cdot}36$ $St=0{\cdot}72\ Re^{-0.30}$; for beds of high D_t/D_p ratio
Ruckenstein[123]	New model and correlation based on others data	$P=1$	—	—	—	Fluidized	—	—	—	—	$Nu=0{\cdot}68\ \varepsilon^{-1.15}\ Re^{0.5}\ Pr^{0.33}$
Sengupta and Thodos[125]	New correlation based on others data	$P=1$	—	—	—	Packed and fluidized	—	0·33–0·778	50–15000	—	$(\varepsilon J_h/f)=0{\cdot}322\Big/\left[\left(\frac{\sqrt{A_p}G}{\mu}\right)^{0.35}-1{\cdot}90\right]$ $\sqrt{A_p}G/\mu > 50$

Sengupta and Thodos[127]	New correlation based on others data	$P=1$	—	—	—	Packed	—	—	95–2500	—	J_h $\varepsilon=2\cdot06/Re^{0\cdot575}$
Bernshtein[130]	S, constant rate drying	Air, $P=?$ $T=?$	Gypsem sphere, grains	1·621–3·10; 1·46	—	Packed	—	0·299–0·395; 0·55	20–1850	~0·6	$Nu=A\ Re^{0\cdot5}$; for spheres $A=0\cdot52$ for $D_p=1\cdot621$ and 1·02 for $D_p=3\cdot1$ $Nu=0\cdot1\ Re$; for grains
Bradshaw and Myers[131]	S, constant rate drying	Air, $P=1$, $T=21$	Kaslin AMT cylinders Celite, Kabsorb, spheres	0·4064-0·5664; 0·47–0·8763	<21	Packed and fluidized 15·24, 30·48	2·54–15·24	0·4–0·8	240–4000	0·708	$J_h=0\cdot5264\ (Re/1-\varepsilon)^{-0\cdot28}$
Chechetkin[132]	Empirical correlation of others data	—	Metallic and non-metallic various	—	—	Packed	—	—	50–1170; 50–2000	—	$Nu=0\cdot025\ Re^{0\cdot89}\ (k_s/k_f)$ for metallic particles (k_s=32–330 kcal/m hr °C) $Nu=0\cdot123\ Re^{0\cdot83}\ (k_s/k_f)$ for non-metallic particles (k_s=1·44–0·11 kcal/m hr °C)
Chen and Churchill[133]	—	Air, $P=1$ T=400–1100	Glass, alumina, steel, Sic spheres grains	0·175–0·625	400–1100	Packed 2× diam.	1·016–7·874	0·35–0·69	—	—	Radiation conductance is reported
Chukhanov[134]	Theoretical	Gases	—	—	—	—	—	—	—	—	$Nu=0\cdot25\ Re^{0\cdot82}$; for $Re<30$ $Nu=\dfrac{0\cdot043\ Re^{0\cdot8}\ (1-Re^{0\cdot7})}{[1+0\cdot88Re^{-0\cdot1}(1\cdot44-0\cdot88\ Re^{-9\cdot1})]}\times\dfrac{(1-0\cdot78\ Re^{-0\cdot2})}{(1\cdot04-0\cdot78\ Re^{-0\cdot2})}$ for $Re>30$
Holman *et al.*[136]	T, step change in induction heating	Water $P<5\cdot0$ T=37·8–93·3	Steel, lead spheres	0·1587–0·4762	37·8–93·3	Fluidized 5·08	58·42	0·50–0·85	6–70	1·9–4·4	$Nu=3\cdot07\times10^{-6}\ (ReF\varepsilon)^2 Pr^{1\cdot5}\ (D_t/D_p)^{0\cdot5}\times(\rho_f/\rho_p)^2$
Littman[137]	T, Frequency response	Air, $P=1$, T=37·8	Copper spheres	0·0716	37·8	Packed 5·08	4·496–8·89	—	—	~0·7	$St=0\cdot2$; $Re=26$

(Contd)

TABLE 1 — SUMMARY OF THE LITERATURE ON HEAT TRANSFER IN FIXED AND FLUIDIZED BEDS (*Contd*)

Author(s)	Experimental technique	Fluid	Particle			Bed characteristics			*Re*	*Pr*	Correlation
			Material and shape	Size cm	Temp. °C	Nature and cross-section cm	Height cm	Void fraction			
McConnachie and Thodos[140]	*S*, constant rate drying	Air, $P=1$, Room temp.	Celite spheres	1·5875	Same as air temp.	Packed & distended 9·378	6·579–8·484	0·416–0·778	235–7285	~0·719	$J_h=1·192/[(Re/1-\varepsilon)^{0.41}-1·52]$
Moore[141]	*S*, induction heating	Water $P=1$, $T=?$	Steel, lead spheres	—	—	Fluidized	—	—	—	~5·0	$Nu=C(ReF\varepsilon)^a Pr^b (D_t/D_p)^{0.5} (\rho_f/\rho_s)^d$
Sengupta and Thodos[145]	*S*, constant rate drying	Air, $P=1$, Room temp.	Celite spheres	1·5875	—	Packed and distended 12·7 × 12·7	17·78	0·444–0·778	95–2500	~0·718	$\varepsilon J_h=2·06/Re^{0.575}$
Solntsev *et al.*[146]	*T*, step input	Air, $P=1$, $T=37·8$	Basalt, silica-gel activated-carbon granular	0·2032–0·6096; 0·4318, 0·3048	37·8	Moving bed 5·842	3·048–12·7	~0·5	380–3500	~0·71	$St=0·095\ Re^{-0.13}$
Vasanova and Syromyatnikov[147]	*S*, induction heating	Air, $P=1$, $T=?$	Copper, aluminium graphite spheres	0·04–0·4	—	Fluidized 8·3	—	—	30–500	~0·7	$Nu=0·316\ Re^{0.8}$; $Nu=0·37\ Re(H_o/D_t)^{-1}$ for true heat transfer coeff.
Elukhin and Starosvitskii[151]	*T*, step input	Air, $P=1$, $T=21·1$–93·3	Steel spheres	0·8686	21·1–93·3	Packed 12·954	240	0·38	225–2250	0·71	$St=0·385\ Re^{-0.2}$
Fujishige[152]	T, cooling of particles	Air, $P=1$ $T=100$	Quartz, Cinder, pyrite, coke, resin granular	—	100	Fluidized	—	—	—	0·7	$Nu=\frac{2·90\times10^{-2}.\phi Re^{0.945}}{(u/u_{mf})^{-0.223}}$ ϕ = function of particle shape

Juveland *et al.*[157]	S, induction heating	Helium, argon $P=1$, $T=227\cdot8$–810 in; 695–1120 out; 140 in, 540 out	ZrC spherical Ar	0·035-0·1651	721–1140	Fluidized 1·905	0·1803-1·3081 (fixed)	0·42 (fixed)	0·23–84	0·71; 0·66	$J_h=0\cdot0603\ Re^{0.173}$
Pavel[167]	*T*, cooling of gas	Air, $P=1$, $T=58$–103	Quartz sand, Cu-Ni catalyst granular	—	<58–103	Fluidized	3·0-11·0 (Static)	—	$G=565$–1435 m/hr 2–12 m/hr	~0·7	$Nu=0\cdot0406\ Re^{1.26}\ (D_p/H)^{0.6}W^{-0.93}$; $2\cdot67 \leqslant W \leqslant 8\cdot5$ W=fluidization index; dimensionless
Sengupta and Thodos[172]	*S*, constant rate drying	Air, $P=1$, T=Room temp.	Celite spheres	1·5875	≈Room temp.	Packed and distended 9·378	—	0·444–0·778	1935–10300	~0·6	$\varepsilon J_h=0\cdot0282$–$0\cdot0122$; $h=18\cdot7$–$66\cdot9$
Shimanskii and Syromyatnikov[174]	*S*, induction heating	Air, Water, $P=1$ $T=?$	Copper, aluminium spheres	0·0428–0·12; 0·23; 0·354	—	Fluidized 5·8	—	—	10–400	0·7–10	$Nu=0\cdot573\ Re\ Pr\ (D/_pH_{fix})$; effective $H/D_p=6$-200 $Nu=1\cdot25\ Re^{1.25}\ Pr^{.059}$; true coeff.
Vasanova and Syromyatnikov[178]	*S*, induction heating	Air, $P=1$, $T=?$	Copper, aluminium spheres	—	—	Fixed and fluidized	—	—	—	~0·7	$Nu=0\cdot316\ Re^{0.8}$; $Re>50$
Gel'perin and Kagan[187]	*T*, cooling of gas	H_2 $P=1$, $T=80$–240 °K	Lead, silica, alumina spheres, granular	—	≈80–240°K	Packed	—	—	40–400	~0·7	$Nu=0\cdot0051\ Re^{1.21}\ Pr^{0.68}\ (D_t\ D_p)^{0.24} \times(\mu_g/\mu_w)^{-0.7} \times (\lambda_g/\lambda_w)^{0.65}$
Holman *et al.*[188]	*S*, induction heating	Water, $P=1$, $T=?$	Steel, lead spheres	—	—	Fludized	—	—	240–14000	~5·9	$Nu=1\cdot28\times10^{-5}\ (Re\ F\varepsilon)^{2.0}\ Pr^{0.67}$ $(D_t/D_p)^{0.5}\times(\rho_f/\rho_p)\ (\mu/\mu_o)^{0.82}$
Kelly[190]	*S*, Freeze drying	Air, $P=1$, $T=26$–37	Peas spherical	0·04–0·06	—	Packed and fluidized	5·0	—	$u=2\cdot5$–7m/sec	~0·6	—
Lindin and Kazakova[194]	*T*, heating of gas	Air, $P=1$, $T=?$	Polymer, slag, corundum sphere, granules	0·04–0·2	—	Packed and fluidized	—	—	5–450	~0·7	$Nu=0\cdot01\ (Re/\varepsilon)^{1.4}$; $5 \leqslant Re \leqslant 120$ $Nu=0\cdot18\ (Re/\varepsilon)^{0.85}$; $120 \leqslant Re \leqslant 450$

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TABLE 1 — SUMMARY OF THE LITERATURE ON HEAT TRANSFER IN FIXED AND FLUDIZED BEDS (*Contd*)

Author(s)	Experimental technique	Fluid	Particle			Bed characteristics			*Re*	*Pr*	Correlation
			Material and shape	Size cm	Temp. °C	Nature and cross-section cm	Height cm	Void fraction			
Rowe and Claxton[199]	*S*, one sphere electrically heated	Air, Water, $P=1$, $T=?$	Copper spheres	—	—	Packed	—	—	—	—	$Nu=A\pm B\ Pr^{1/3}\ Re^{n}$; $[(2-3n)/(3n-1] = 4{\cdot}65\ Re^{-0.23}$ $A=2/[1-(1-\varepsilon)^{1/3}]$; $B=2/3\ \varepsilon$
Vasanova and Syromyatnikov[205]	—	Air, $P=1$, $T=?$	—	—	—	Fluidized	—	—	80–500	—	$Nu=0{\cdot}001185\ Re^{1.6}$
Baldwin *et al.*[209]	*S*, induction heating	Water, $P=1$ $T=?$	Spheres	4·9112	—	Packed 30·48x 30·48	—	0·48, 0·26	3000–70000	~5·8	$J_h=0{\cdot}99Re^{-0.33}$; cubic packing $J_h=0{\cdot}94Re^{-0.30}$; dense cubic packing
Binder and[212] Kondukov	T, cooling of particles	Air, $P=1$ $T=?$	Steel, glass, silica-gel spheres	0·045–0·32	600–700°K	Fluidized	—	—	—	~0·7	$h=0{\cdot}145\ Fr^{-0.24}\ (1-1{\cdot}12\ H_o/D_p)\times (\rho_{m-}-\rho_g\ \rho_g)^{0.4}$; $30 < Fe < 5300$; H_o/D_p =7–50
Chang and Wen[216]	*T*, cooling of particles	Air, $P=1$, $T=51{\cdot}7$–$102{\cdot}2$	Aluminium steel, brass spheres	0·4762–0·635	26·7–148·9	Fluidized 5·08	—	0·425–0·879	580–5000	~0·7	$J_h=0{\cdot}097(Re/1-\varepsilon)^{-0.502}Ar^{0.198}$
Littman and Stone	*T*, Frequency response	Air, $P=1$ $T=?$	Copper spheres	0·0599	—	Fluidized	5·08	—	—	~0·7	—
Lyuboshits and Kuts[239]	T, cooling of gas	Air, $P=1$ $T=?$	Wheat ellip-soidal	—	—	Moving bed 20 × 20 cm	—	—	18–100	~0·8	$Nu=0{\cdot}043\ Re^{0.78}$
Safryan *et al.*[250]	S, constant rate drying	Air, $P=1$, $T=?$	Ca-meta-silicate granules	—	—	Fluidized	—	—	—	~0·7	$Nu=K\ Re^{a}\ Pe^{b}\ (D/H_o)^{c}\ (H/H_o)^{d}$
Schluender[252]	S, one sphere heated	Air, $P=1$ $T=?$	Brass, glass sphere	0·2–1·5, 0·1–2·5	—	Packed 2·5–7·0	—	—	—	~0·7	—

Themelis and Yannopoulos[255]	S, reduction of CuO (free by suspended single particle	H_2, $P=1$ $T=?$	CuO granular	—	—	Fluidized	—	—	—	~0·8	$Nu=2+0·552\ Re^{0·5}\ Pr^{0·33}$
Zabrodsky and Zhitkevich[261]	—	Air, $P=1$	Sphere	5·0	—	Packed	—	—	50–34000	~0·7	$Nu=2+1·18\ Re^{0·53}$; $50<Re<3000$ $Nu=0·263\ Re^{0·73}$; $2000<Re<40000$ (for dense packed) $Nu=0·87\ (\varepsilon_d/\varepsilon_l)-0·19Re$ (for loosely packed)
Healy[271]	T, Frequency response	Air, $P=1$ $T=?$	Copper, glass spheres	—	—	Packed and fluidized 5·08	—	—	4–55	0·7	—
Malling and Thodos[278]	S, constant rate evaporation	Air, $P=1$, ≈Room temp.	Celite spheres	0·617–0·625	≈Room Temp.	Packed & distended 3·72″	6×625″	0·366–0·794	180–8500	0·712–0·714	$\varepsilon^{11·9}\ J_h=0·7630/Re^{0·472}$
Rabinovich *et. al.*[285]	T, cooling of gas	N_2, $P=1$–21, $T=100$–400 (inlet)	Silica-gel granular	0·25	—	Fluidized 4·0	4·0 (Static)	—	—	~0·7	$Nu=0·055\ Re^{0·77}(\rho/\rho_\circ)^{0\,2}$
Uemaki and Kugo[289]	—	Air, $P=1$ $T=?$ 6–8;	Coke, glass, pumiee-stone, aluminium silica, wheat granules, spheres	4–20; 5–10; 6–10; 6–10; 0·41	—	Spouted bed 9·2	—	—	—	~0·7	$Nu=5·0\times10^{-4}\ Re^{1·46}\ (\mathbf{u}/\mathbf{u}_{ms})^{1·030}$ where $\mathbf{u}_{ms}$ = used for minimum spouting velocity
Gillespie *et al.*[296]	S, heating of air	Air, $P=1$ $T=?$	Sphere	—	—	Packed 30·48×30·48	88·9	—	120–1700	~0·7	—
Littman *et al.*[298]	T, Frequency response	Air, $P=1$	Copper, glass, lead spheres	0·0503–0·203	—	Packed	—	—	1·92–992	0·708	—
Mann and Feng[300]	T, heating and cooling	Air, $P=1$, $T=54·4$–140·6	Glass, silica-gel, alumina sphere, granular	0·255–0·6121	54·5–140·6	Fluidized 5·08, 10·16	2·032–40·64 (static)	—	10–2200	0·7	—

(Contd)

TABLE 1 — SUMMARY OF THE LITERATURE ON HEAT TRANSFER IN FIXED AND FLUIDIZED BEDS (*Contd*)

Author(s)	Experimental technique	Fluid	Particle			Bed characteristics			*Re*	*Pr*	Correlation
			Material and shape	Size cm	Temp. °C	Nature and cross-section cm	Height cm	Void fraction			
Petrovic and Thodos[302]	*S*, constant rate drying	Air, $P=3$, $T=12\cdot2$–$29\cdot3$	Celite sphere	0·1831–0·3086	—12·2–29·3	Fluidized 9·4488, 11·271	—	0·426–0·753	100–1000	0·72	$J_h=1\cdot12\ Re^{-0.363}$
Sechenov *et. al.*[303]	—	CO_2, N_2, mixture, $P=5$-20 $T=?$	Sodalime, granules	0·032	—	Fluidized 4·0	20·0	—	—	~0·8	—
Bradshaw *et. al.*[315]	—	Air, N_2 $P=1$ $T=?$	Steel, alumina, hematite spheres, pellets	0·9525–2·54	20–80	Packed 40·0	—	—	150–600	~0·7	$J_h=0\cdot495\ Re^{-0.375}$
Gliden and Crawfield[322]	*T*, cooling of solids	Air, $P=1$ $T=?$	Alumina granules	0·12	600	Packed	—	—	2–25	0·69	$Nu=0\cdot36\ Re^{0.94}$
Kato and Wen[327]	New correlations based on others data	Gases, $P=1$ $T=?$	—	—	—	Packed & Fluidized	—	—	0·1–1000	~0·7	$Nu=1\cdot05\ Pr^{1/3}\ [Re(D_p/L)^{0.6}]^{1.1}$; $0\cdot1 \leqslant Re(D_p/L)^{0.6} \leqslant 2\cdot5$ $Nu=1\cdot5\ Pr^{1/3}\ [Re(D_p/L)^{0.6}]^{0.63}$; $2\cdot5 \leqslant Re(D_p/L)^{0.6} \leqslant 10^3$
Bhattacharyya and Pei[342]	Microwave heating	Air, $P=?$ $T=?$	Fe_2O_3 Spheres, cylinders	0·32, 0·508	—	Fixed	—	—	—	—	$(J_h)_{fp}=0\cdot043\ [Ar/Rem^2]^{1/4}$ for $0\cdot02 < Ar/Rem^2 < 10$
Bhattacharyya and Pei[346]	Microwave heating	Air, $P=4$, $T=21\cdot94$ 83·33	Fe_2O_3 Spheres, cylinders	0·32–0·762	35·72–104·72	Fixed	4·445–4·7625	—	108–833; *Rem*-2.2–1371	—	$(J_h)_{fp}=0\cdot018\ [Ar/Rem^2]^{1/4}$; for $4\cdot2 < Ar/Rem^2 < 103$
Kmiec[347]	Constant rate drying	Gas, $T=50$	Silicagel, activated coal spheres	0·874–3·315 mm	—	Spouted bed	4·32–11·4	—	—	—	$Nu=0\cdot897\ Re^{0.464}\ Pr^{0.333}\ Ar^{0.116} \times (T_g\gamma/2)^{0.813}\ (H_o/D_p)^{-1.19}\ \phi^{2.26}$; $(J_h/J_d)_s=1\cdot082\ Re^{-0.223}\ Ar^{0.031} \times (T_g\gamma/2)^{-9.15}\ (H_o/D_p)^{0.037}\ \phi^{0.507}$ for $\gamma \rightarrow 30°$ to 90°

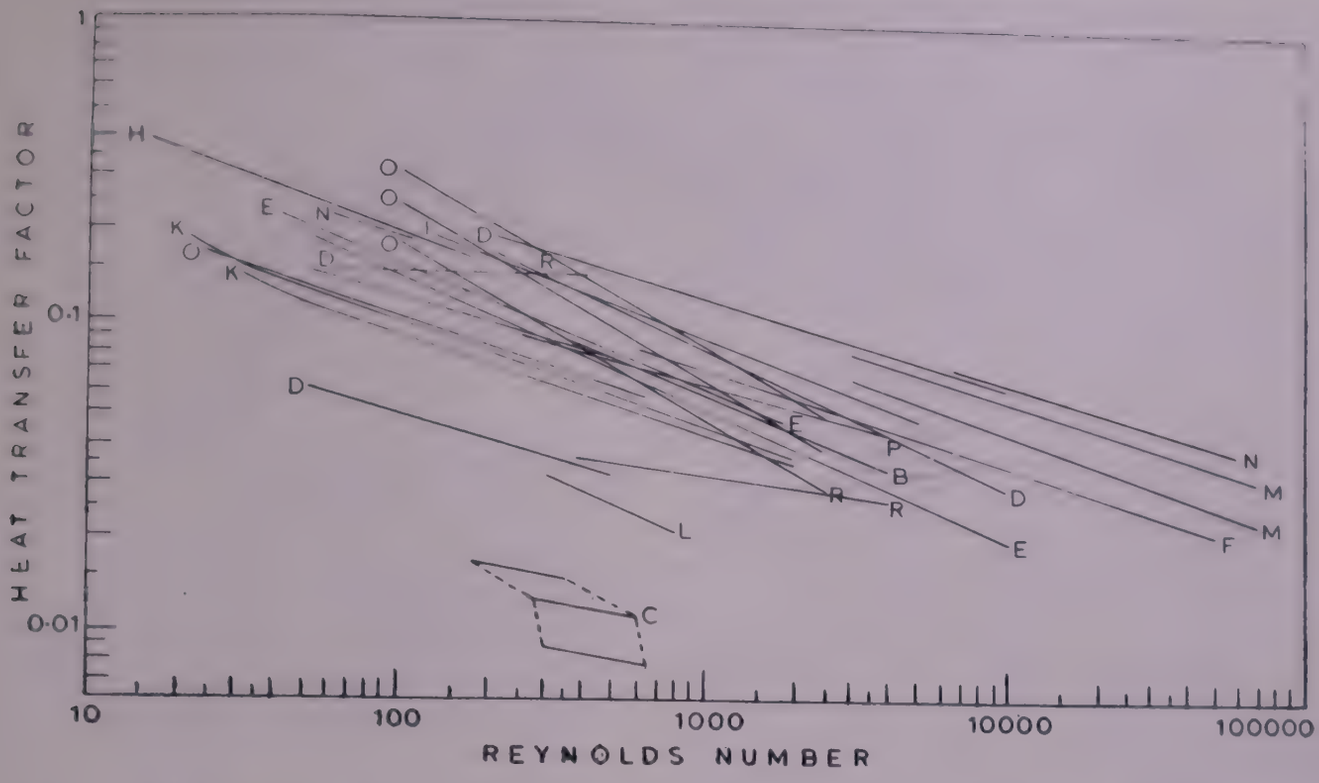

Fig. 1 — Heat transfer in fixed beds [A, Saunders and Ford[9]; B, Gamson *et al.*[13]; C, Norton[17]; D, Lof and Hawley[21]; E, Taecker and Hougen[22]; F, Denton[28A]; G, Lydersen[26]; H, Satterfield and Resnick[36]; I, Ball[52]; J, Baumiester and Bennett[53]; K, Glaser and Thodos[57]; L, Lankashire *et al.*[68]; M, Baldwin[91]; N, Wadsworth[101]; O, Sengupta and Thodos[125]; P, Bradshaw & Myers[131]; Q, Littman[137]; and R, Solnetsev *et al.*[146]]

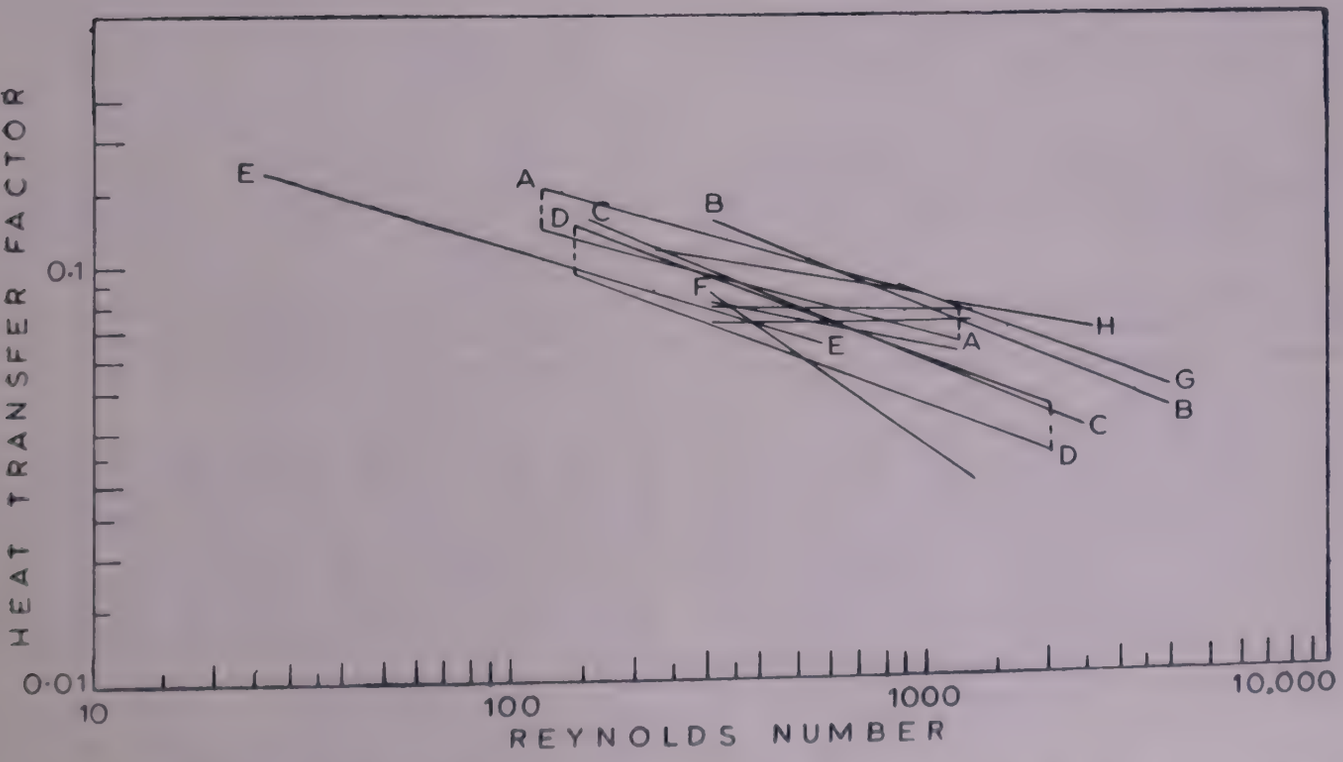

Fig. 2 — Heat transfer in packed beds [A, Furnas[3-5]; B, Glaser[19]; C, Dayton *et al.*[29]; D, Glaser[40]; E, Coppage and London[42]; F, Galloway *et al.*[48]; G, Meek[121] and H, Elukhin and Starosvitskii[151]]

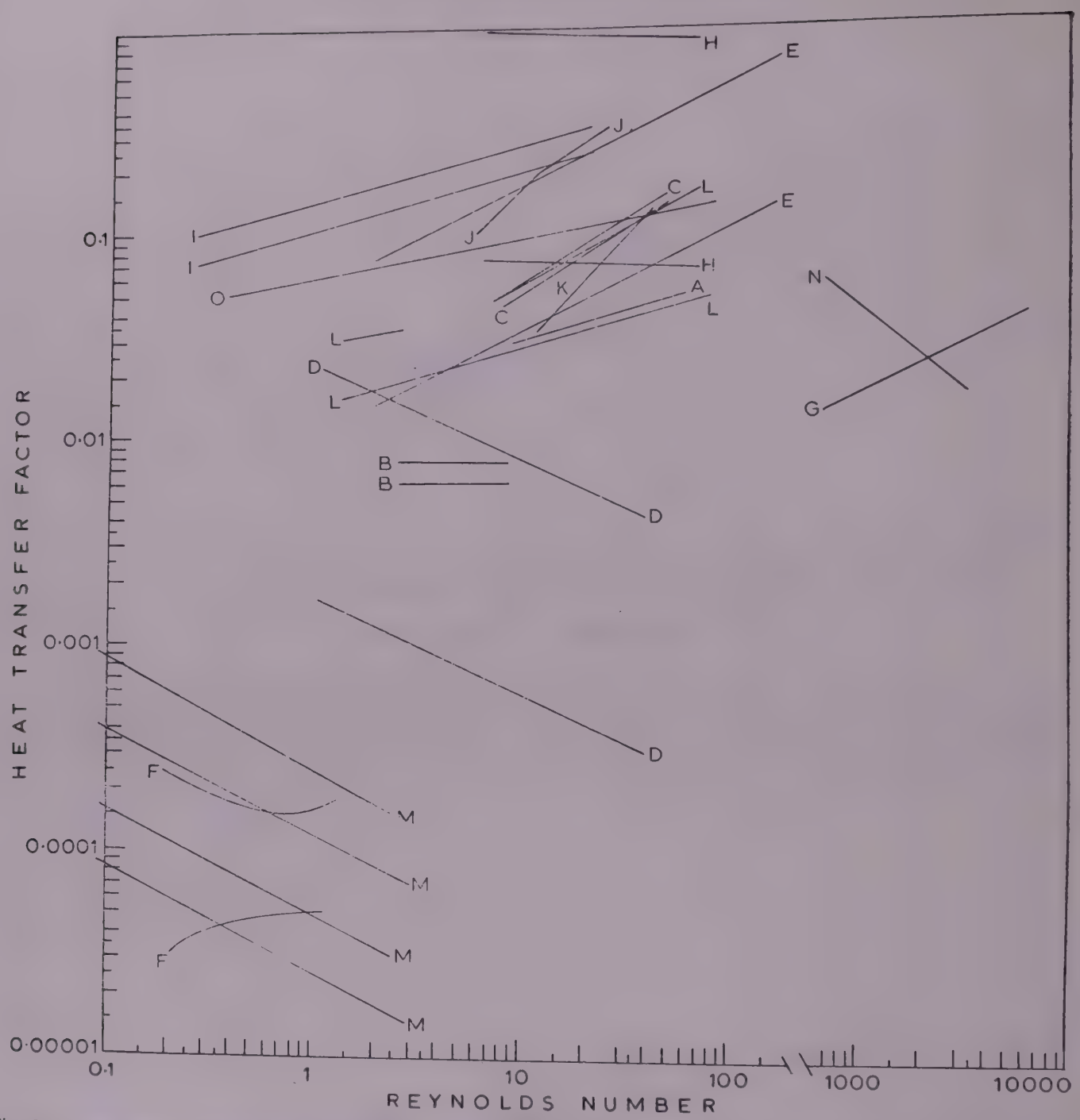

Fig. 3 — Heat transfer in fluidized beds [A, Kettenring *et al.*[25]; B, Anton[32]; C, Walton *et al.*[31]; D, Wamsley and Johnson[37]; E, Shakhova *et al.*[35,51]; F, Fritz[44]; G, Rozental[61]; H, Heertjes[67]; I, Richardson and Ayers,[71]; J., Donnadieu[80]; K, Sunkoori and Kaparthi[87]; L, Frantz[96]; M, Ferron and Watson[109]; N, Bradshaw and Myers[131]; and O, Juveland *et al.*[157]]

134, 141, 146-148, 152, 153, 168, 173, 175, 179, 191 200, 206, 213, 217, 238, 240, 251, 253, 262, 272, 279, 290, 297, 299, 301, 303, 316, 324). Occasionally, other gases like argon (ref. 158), carbon dioxide (ref. 31, 38, 58, 72, 93), helium (ref. 158), hydrogen (ref. 55, 58, 188, 256,), nitrogen (ref. 93, 286, 304, 316), steam (ref. 93), gas mixture (ref. 304), and certain other gases (ref. 37, 77, 328, 343), have also been used. Data with liquids are meagre and are confined only to water (ref. 88, 92, 142, 175, 189, 301).

Varied particle shapes have been studied. These include spheres (ref. 3, 9, 13, 17, 19, 26, 30, 37, 38, 40, 43, 46, 49, 53, 52, 58, 59, 72, 73, 79, 85, 92, 98, 102, 103, 114, 116, 122, 134, 137, 138, 141, 142, 146, 148, 152, 158, 173, 175, 179, 188, 189, 191, 200, 210, 213, 217, 238, 262, 272, 279, 290 297, 299, 301, 303, 316, 341, 343, 348), cubes (ref. 58, 62), cylinders (ref. 13-15, 58, 62), commercial packings (ref. 22, 34, 41, 62, 103), pellets (ref. 59, 316), and granular solids (ref. 21, 25, 32-36, 38, 41, 52, 66, 73, 80, 82, 88, 94, 98, 110, 134, 147, 153, 168, 188, 251, 253, 256, 286, 301, 304, 324).

Most of the workers have correlated their results in terms of the Chilton-Colburn J_h factor and particle Reynolds number. Nusselts number has also been used by many investigators. In a few cases, heat transfer coefficient has been directly correlated with the operating variables, the mass flow rate, particle

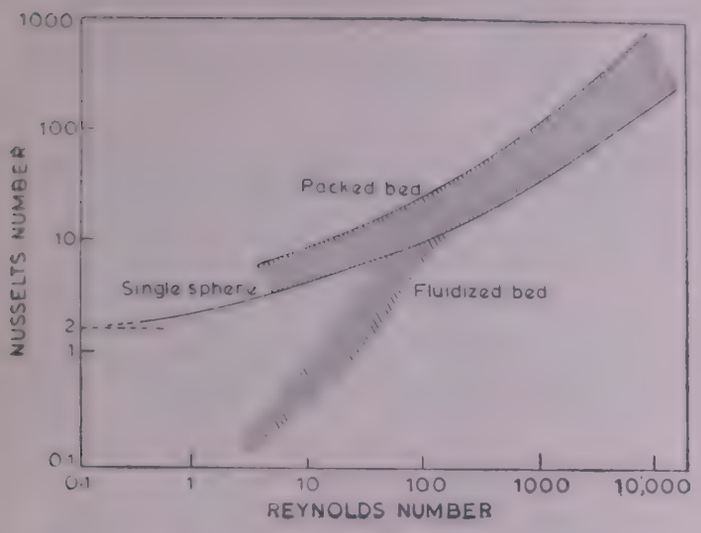

Fig. 4 — General trend in particle fluid heat transfer

diameter, etc. New dimensionless groups have been introduced by many workers. The various terms and dimensionless groups are not always the same and depend upon the definition chosen by the investigator. For example, particle Reynolds number defined by

$$Re = D_p V\rho/\mu \quad \ldots(1)$$

$$Re' = D_p V\rho/\mu \quad \ldots(2)$$

and $$Re'' = D_p V\rho/\mu\ (1-\varepsilon) \quad \ldots(3)$$

have been used frequently. Even the particle diameter used in the various dimensionless groups is not the same. Some workers have defined it as the diameter of the sphere having the same volume as the particle, and same as the diameter of a sphere having the same surface area as the particle.

A majority of work rs have proposed more than one correlation, which cover different ranges of particle Reynolds number and are often valid within the range covered. Some have tried to improve their correlations by including new variables, such as D_P/D_T, D_P/H or shape factor. This lack of uniformity in the reporting of the results makes a comparison of the various studies difficult. However, some of the correlations for fixed and fluidized beds are compared separately in Figs 1-3. Poor agreement between most of the reported results is evident from these figures.

In most of the measurements, the total area of the bed has not been effective in transferring heat and only a small undetermined fraction of the particles in the bed has been actually involved in the heat transfer process. The problem of proper temperature distribution and difference is a source of much difficulty with fluidized bed measurements. The variation in data cannot be attributed to shortcomings in the experimental techniques alone, but also to the particular nature of the fluidized beds and fluidizing conditions.

The discrepancies in the results of various workers may also be due to some additional factors also. In analysing the experimental results on heat transfer in fixed and fluidized beds, a uniform flow velocity over the entire cross-section of the bed has been assumed by many workers, and transport of heat by conduction and mixing in the direction of the flow is usually neglected with respect to convective transport. But this is not true in many cases. Bed inhomogeneity, which is often the case with beds of large particles, gives rise to non-uniform flow distribution leading to radial temperature gradients.

Errors in the measured driving force, bed height, surface area, etc. and inaccuracies in the physical properties like viscosity, thermal conductivity, fluid heat capacity, etc. may also add to the divergence in the reported values.

For resolving these issues, it would be advantageous to obtain new data particularly in the fluidized bed region. These measurements must consider systematically the effects of all the variables affecting the transfer rate. Attention must be paid to the manner in which the bed is formed and whether or not it changes its geometry during the course of the experiment and the desired physical properties must be known with sufficient accuracy. In the low Reynolds number region, new data are needed for both fixed and fluidized beds. As suggested by Chechetkin (ref. 133), low rate data are likely to depend upon the thermal condcutivity of the solid forming the bed and its effect should be taken into account during the analysis of low rate results. In both the beds, data with fluids of widely varying Prandtl number will be a welcome addition. Lack of uniformity in the reporting of the results suggests the need for prescribing a standard method of obtaining and analysing the experimental results.

Summary

Literature on particle-fluid heat transfer in fixed and fluidized beds has been reviewed. Certain factors which should be considered in the future studies on the subject have also been pointed out.

Acknowledgement

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Nomenclature

a	=	constant used in reference 40
A	=	constant used in references 11, 92, 130, 199
A_p	=	geometric surface area of a single particle (L^2)
Ar	=	Archimedis number = $(D_p^3 g/\nu^2)$ $(\Delta T\beta/T)$, (dimensionless)
b	=	constant used in reference 141
B	=	constant used in reference 199
c	=	constant used in reference 142
C	=	constant used in reference 81
C_p	=	specific heat at constant pressure; $(L^2/t^2\theta)$
d	=	constant used in reference 142
d_e	=	equivalent diameter (L)
D	=	diffusion coefficient (L^2/t)
D_c	=	column diameter (L)
D_p	=	particle diameter (L)
D_t	=	column diameter (L)
f	=	area availability factor used in ref. 125 (dimensionless)

f = function used in ref. 79
f = friction factor used in ref. 125
Fe = Fedorov number used in ref. 24
Fr = Froude number = (u^2/gD_p); (dimensionless)
Fr' = modified Froude number = $(V^2/\varepsilon^2_f\ D_p)$; (dimensionless)
F = function of void fraction used in refs. 136, 141
g = acceleration due to gravity (L/t^2)
G = mass flow rate (M/L^2t)
Gmf = minimum fluidization mass flow rate (M/L^2t)
h' = heat transfer coefficient used in ref. (21); $(M/t^3\theta)$
h = heat transfer coefficient $(M/t)\theta$
H = bed height (L)
H_o = height of the stationary bed (L)
H_T = height of transfer unit used in ref. 14 (L)
J_d = mass transfer factor = $(kc/u)N_{Sc}^{2/3}$; (dimensionless)
J_h = heat transfer factor = $(h/c_pG)Np_r^{2/3}$(dimensionless)
$(J_h)_{fp}$ = heat transfer factor used in refs. 343, 347 (dimensionless)
k_c = mass transfer coefficient (L/t)
k_f = thermal conductivity of fluid $(ML/t^3\theta)$
k_s = thermal conductivity of solids $(ML/t^3\theta)$
K = a constant used in ref. 251 (dimensionless)
L = bed height (L)
L = lenght, a fundamental dimension (L)
m = a ratio used in ref. 59, = $(V_{practical}/V_{heating\ zone})$ (dimensionless)
m_M = a constant used in ref. 82 (dimensionless)
M = mass, a fundamental dimension (M)
N = fluidization index used in ref. 36 (dimensionless)
Nu = Nusselt number = $(h\ D_p/k_f)$ (dimensionless)
P = pressure $(M/L\ t^2)$
Pe = Peclet number, = $(u\ D_p/D)$ (dimensionless)
Pr = Prandtl number = $(\mu_f\ C_p/k_f)$ (dimensionless)
Re = Reynolds number = $(D_p u\rho_f\ /\mu_f)$ (dimensionless)
Re' = Reynolds number = $(D_p\ u\ \rho_f/\mu_f\ \varepsilon)$
Rem = Reynolds number = $[(D_p u\rho_f/\mu_f\ (1-\varepsilon)]$(dimensionless)
Sc = Schmidt number = $(\mu_f/\rho_f D)$ (dimensionless)
St = Stanton number, = (h/C_pG) (dimensionless)
t = time, a fundamental dimension (t)
T = temperature (θ)
T_g = tangent of angle of conical base
u = superficial flow velocity (L/t)
u_{ms} = minimum spouting velocity (L/t)
U = heat transfer coefficient $(ML/t^3\theta)$
V = flow velocity (L/t)
V_p = volume of bed particle used in ref. 59 (L^3)
V_h = volume of heating zone used in ref. 59 (L^3)
W = fluidization index used in ref. 168 (dimensionless)
β = thermal coefficient of volumetric expansion (θ^{-1})
γ = conical base angle (degree)
ε = void fraction of the bed (dimensionless)
ε_d = void fraction for dense packed bed (dimensionless)
ε_l = void fraction for loose packed bed (dimensionless)
ε_o = void fraction at the inlet of bed (dimensionless)
θ = temperature, a fundamental dimension (θ)
λ_g = thermal conductivity of gas $(ML/t^3\theta)$
λ_w = thermal conductivity at wall $(ML/t^3\theta)$
μ_f = fluid viscosity (M/Lt)
μ_g = gas viscosity (M/Lt)
ρ = density of gas at elevated pressure (M/L^3); ρ_f density of the fluid; ρ_m density of solid; ρ_o density of gas at atmospheric pressure; ρ_p density of particles; ρ_s density of solid
ϕ = function of particle shape used in ref. 153 (dimensionless)
ϕ = shape factor used in ref.3, 348 (dimensionless)
ν = kinematic viscosity (L^2/t)

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Heat Resistant Explosives

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THERE is immense need in industry for explosive compositions which are safe, reliable and stable at elevated temperatures. For example, it is sometimes necessary to shoot explosive devices in hot oil wells at temperatures which may reach as high as 200°-300°C. In the steel industry, open hearth furnaces are tapped with explosive shaped charges in tap holes at temperarature above 500°C. Using the explosives available at present which have the best possible thermal properties, it is necessary to jacket the shaped charges with heavy insulation. Even so, the charge must be initiated within 3-4 min from the time it is set in place or it may fail due to thermal stability. There is also a growing demand in connection with space programmes for explosive compounds which are stable at elevated temperatures and low pressures. The explosive stores carried externally on high speed aircraft at low altitudes are subjected to aerodynamic heating, which may raise the temperature of the filling above 80°C, so that the Torpexes (RDX/TNT/Al) and other conventional explosives are unsuitable for such stores. Setting aside anything which might be done to insulate the filling from casing, it is necessary to seek explosives which are stable at high temperature.

Explosives with improved high temperature properties, usually called 'Heat Resistant Explosives' have emerged to meet such requirements. Nitro compounds have been found to be very useful as heat resistant explosives. These compounds have received special attention[1-5] because of their ability to withstand the high temperatures and low pressures encountered in space applications. No doubt, the manufacture of these explosives is likely to be on kilogram rather than tonne scale, but the application is highly critical. Sometimes, even complex synthetic routes can be adopted, provided the product exhibits the requisite properties, a low vapour pressure and the ability to function satisfactorily after appropriate environmental trials, which may include heating at temperatures as high as 250°C. A few explosives having these properties are listed in Table 1.

Bicyclic nitroaromatics, hexanitrostilbene (HNS) and diaminohexanitrodiphenyl (DIPAM) are in use for achieving stage separation in space rockets and for siesmic experiments on the moon[6]. Single aromatic ring compounds, such as *m*-diaminotrinitrobenzene (DATB) and triaminotrinitrobenzene (TATB) have also been found to be of practical value in various space applications.

There has been speculation about the relationship between the exceptional thermal stability of these compounds and their molecular structure. Thermal decomposition studies show that the stability is associated with high melting point and low vapour pressure and there is evidence that the rates of decomposition are enhanced when substances are in liquid or vapour phase; they are in higher energy level when molten or vapourized[7].

Solid state physical structure appears to be as

TABLE 1 — HEAT RESISTANT EXPLOSIVES

Explosive	Chemical name	M.P. °C	Crystal density g/cm³	Velocity of detonation km/sec	Detonation pressure (calc.) k bars
DATB	1,3-Diamino-2,4,6-trinitrobenzene	286	1·84	7·50	260
TATB	1,3,5-Triamino-2,4,6-trinitrobnzene	350 (decomp.)	1·94	7·80	290
HNS	2,2′,4,4′,6,6′-Hexanitrostilbne	318	1·74	7·00	215
DIPAM	3,3′-Diamino-2,2′,4,4′,6,6′-hexanitrobiphenyl	304	1·79		
TACOT	Tetranitro-2,3:5,6-dibenze-1,3a,4,6a-tetraazapentalene	410	1·85	7·20	245

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significant as chemical constitution in determining the stability of explosives, but apart from crystal structure determinations on lower molecular weight compounds, such as diaminotrinitrobenzene[8], there is little information available on the magnitude of molecular interactions or crystal lattice effects in these remarkable explosives.

Nitro Derivatives of Benzene

1,3-Diamino-2,4,6-trinitrobenzene (DATB) (III) and 1,3,5-trinitro-2,4,6-triaminobenzene (TATB) (IV) have qualified as heat resistant explosives among the various nitro derivatives of benzene.

Several complicated procedures for the synhteses of diaminotrinitro benzene (DATB) (III) have been reported. In one of these, the synthesis is accomplished[9–11] by vigorously nitrating *m*-dichlorobenzene (I) at elevated temperatures. 1,3-Dichloro-2,4,6-trinitrobenzene (II) thus obtained is aminated in methanol to yield DATB (Fig. 1). The yield obtained has not been reported.

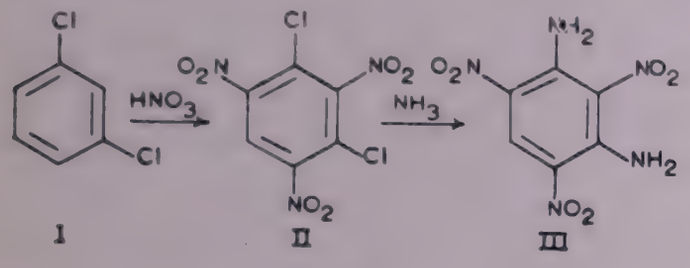


Fig. 1

The second approach[12] comprises the preparation of dipyridinium styphnate from styphnic acid in 94% yield. Compound II can be obtained in 98% yield by allowing phosphorous trichloride and dipyridinium styphnate to react directly at steam bath temperature. DATB was obtained by the amination reaction (mentioned above) in 97% yield. The overall yield of III is considerably better than that obtainable by the existing procedures.

DATB is a lemon-yellow crystalline substance. It is fairly stable up to within a little of its melting point, decomposing at the rate of less than 1% per hour at 260°C, but it transforms to crystal form of lower density at 216°C, which temperature, therefore, represents the upper limit of its utility. The use of DATB in high explosive compositions has been described in several patents[13,14].

1,3,5-Trinitro-2,4,6-triaminobenzene (TATB) (IV) is prepared readily[15] from aniline by the route shown in Fig. 2. It is a yellow-brown substance decomposing rapidly just below the melting point; but it has excellent thermal stability in the range 260-290°C, which represents the upper temperature limit at which it may be used.

Nitro Derivatives of Diphenyl

Among the nitro derivatives of diphenyl, 3,3′-diamino-2,2′,4,4′,6,6′-hexanitrodiphenyl (DIPAM) (VIII) has been found to be a thermally stable explosive. Oesterling *et al.*[16] described a method in which the starting material is *m*-haloanisole. The general reaction sequence is shown in Fig. 3.

The above method of preparing DIPAM comprises (a) nitration of a *m*-haloanisole (V) with a mixture of nitric acid and oleum to obtain 3-halo-2, 4,6-trinitroanisole (VI); (b) condensation of two molecules of VI by reacting it with a slurry of copper powder and a diluent to obtain 3,3′-dimethoxy-2,2′,4,4′,6,6′-hexanitrodiphenyl (VII); and (c) amination of VII to 3,3′-diamino-2,2′4,4′,6,6′-hexanitrodiphenyl (VIII) by introducing ammonia into a solution comprising

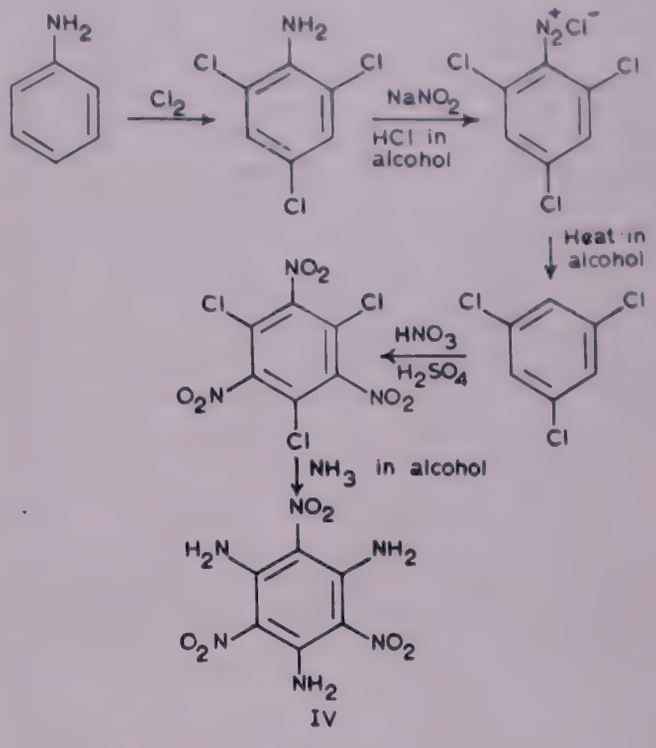


Fig. 2

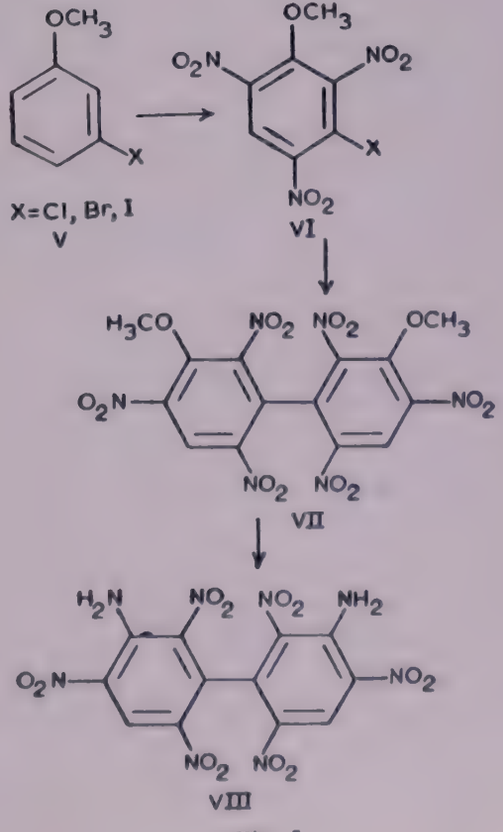


Fig. 3

VII and a diluent which may be methanol, tetrahydrofuran or xylene-methanol-tetrahydrofuran mixture.

In addition to the ability of this explosive to withstand high temperatures, it is extremely insensitive to electrostatic discharge, requiring more than 32,000 J for initiation.

Nitro Derivatives of Dibenzyl and Stilbene

Nitro derivatives of dibenzyl and stilbene are of considerable importance for two reasons: (i) Some of them are produced by the nitration of toluene in the course of production of trinitrotoluene (TNT) as a result of the oxidation of CH_3 group; and (ii) some of them show very high melting points and can be regarded as classical examples of explosives resisting high temperatures.

Nitro derivatives of dibenzyl — 2,2′,4,4′,6,6′-Hexanitrodibenzyl, (m.p., 218°C) (IX) was obtained by Will[17] by nitrating 4,4′-dinitrodibenzyl. He also claimed to have obtained it by the alkaline oxidation of TNT. A substance of the same melting point was obtained by Rinkenbach and Aaronson[18] as a by-product of the nitration of 2,2′,4,4′-tetranitrodibenzyl with fuming sulphuric acid and fuming nitric acid at 85° for a few days. The main product of nitration was claimed to be pentanitrodiphenyl ethanol [α-2, 4,5-trinitrophenyl-β-2,4-dinitrophenyl hydroxyethane] (X) (m.p., 187°) (Fig. 4).

Blatt and Rytina[19] re-examined the findings of the earlier workers. They nitrated dibenzyl and 4,4′-dinitrodibenzyl using 100% nitric acid and obtained 2,2′,4,4′-tetranitrodibenzyl (m.p., 171-72°) with 90% yield of the crude product. The product could not be nitrated further unless it was subjected to vigorous nitration conditions, i.e. heating it with nitrating mixture [composed of nitric acid (90% HNO_3), sulphuric acid (95% H_2SO_4), and oleum (15% SO_3)] on steam bath for 7 hr, resulting in the formation of 2,2′,4,4′,6-pentanitrodibenzyl (m.p., 187-88°) and a relatively small amount (~10%) of hexanitrodibenzyl (IX).

Nitration of pentanitrodibenzyl with the same nitrating mixture for 16 hr yielded 30% of hexanitrodibenzyl (IX) and unchanged pentanitrodibenzyl. Compound IX, when crystallized from acetic acid, had m.p. 213-215°. Shipp and Kaplan[20] nitrated dibenzyl using potassium nitrate in 30% oleum in the temperature range 60-120°C for 30 hr and obtained IX in 46·5% yield. After crystallization from hot acetone and water, it melted at 218-20°C.

Neither Blatt and Rytina nor Rinkenbach and Aaronson were able to obtain hexanitrodibenzyl (IX) by the alkaline oxidation of 2,4,6-trinitrotoluene (TNT). However, this was achieved by Shipp and Kaplan[20], who found that TNT could be oxidized to hexanitrodibenzyl or hexanitrostilbene using sodium hypochlorite as the oxdizing agent. Thus, the observation of Will[17] proved to be correct.

A similar process[20] consisted in reacting nitro derivatives of benzyl halogenide with trinitrotoluene in sodium hydroxide. In tetrahydrofuran (THF), 2,4,4′,6-tetranitrodibenzyl (XI) (m.p., 179-80°) and 2,2′,4′,6,6′-pentanitrodibenzyl (XII) (m.p., 155°C) were obtained (Fig. 5).

Nitro derivatives of stilbene — Direct nitration of stilbene does not furnish its nitro derivatives, as the double bond is highly vulnerable and oxidation can occur readily. A number of methods are available for preparing nitrostilbene, the starting materials being nitro derivatives of benzyl halogenides or of toluene.

Nitration of stilbene — Challenger and Clapham[21] nitrated 2,4,6-trinitrostilbene with a mixture of nitric acid (*d*, 1·41) and sulphuric acid at 100°C for 2 hr and obtained 2,4,6,2′,4′-pentanitrostilbene (m.p., 198°). A stronger nitrating mixture composed of anhydrous nitric acid (*d*, 1·5) and sulphuric acid at 100°C yielded 2,4,6,2′,4′-pentanitrobenzil (XIII) (m.p., 260°C). Blatt and Rytina[19] nitrated 2,2′,4,4′-tetranitrostilbene by heating it with nitric acid (90% HNO_3), sulphuric acid (95%) and oleum (15% SO_3) on steam bath for 7 hr and obtained 2,2′,4,4′-tetranitrobenzil (XIV) (m.p., 222°C).

Preparation from nitro derivatives of toluene and benzaldehyde and its derivatives — This type of reaction was first described by Thiele and Escales[22]. On

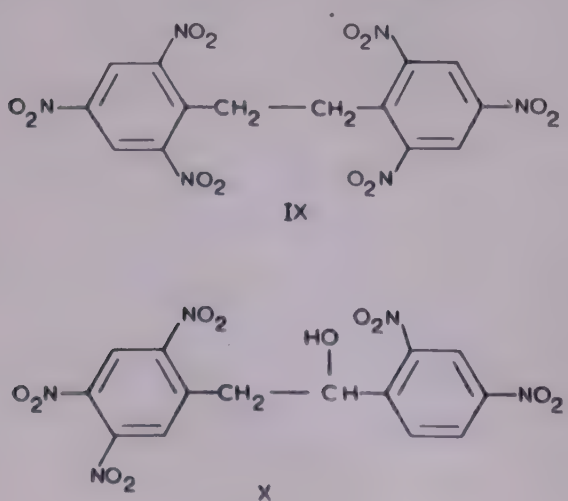


Fig. 4

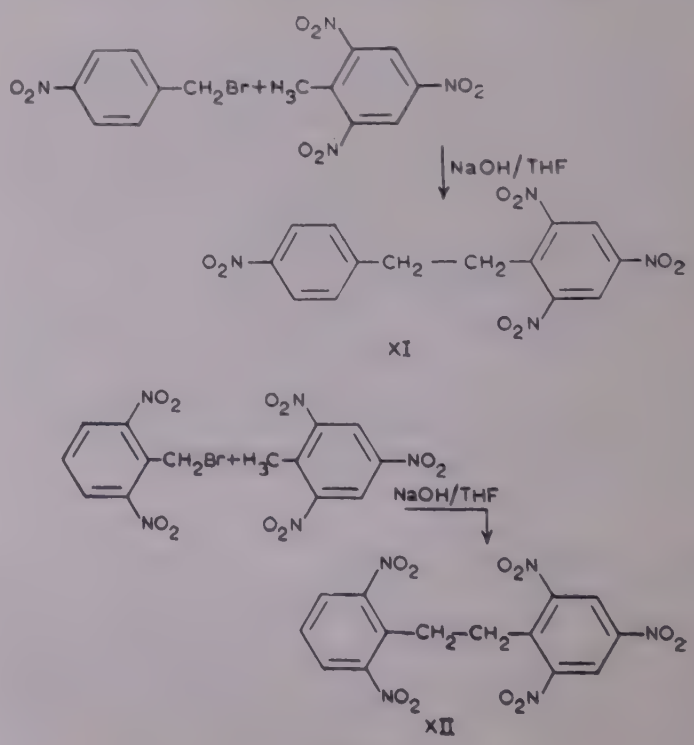


Fig. 5

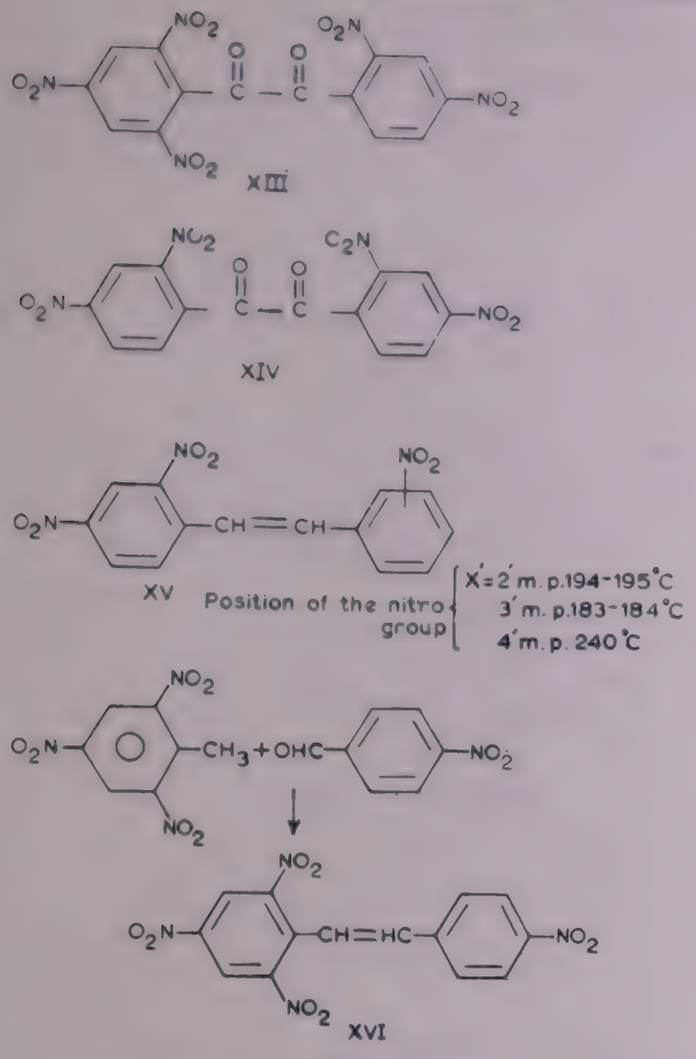


Fig. 6

heating a mixture of 2,4-dinitrotoluene and nitrobenzaldehyde at 160-70°C and allowing the reaction mixture to rest for 2 hr, they obtained all the three possible isomers of 2,4,4′-trinitrostilbene (XV) using *o*-, *m*- and *p*-nitrobenzaldehyde.

Ullman and Gschwind[23] obtained, in a similar way, 2,4,6,4′-tetranitrostilbene (XVI) (m.p., 196°) from trinitrotoluene and *p*-nitrobenzaldehyde (Fig. 6).

Shipp[24] tried the same reaction between trinitrotoluene and trinitrobenzaldehyde and obtained hexanitrostilbene in poor yield.

Preparation from nitrobenzyl halogenides — This method consists in reacting nitrobenzyl halogenides with alcoholic potassium hydroxide. The reaction was described for the first time by Krassusky[25], who obtained 2,4,2′,4′-tetranitrobenzyl (m.p., 266-67°C) by warming 2,4-dinitrobenzyl chloride with potassium hydroxide in ethanol. The reaction did not seem to be successful when 2,4,6-trinitrobenzyl bromide was used as the starting material. Reich *et al.*[26] described the preparation of hexanitrostilbene (m.p., 211°C) by treating trinitrobenzyl bromide with boiling alcoholic potassium hydroxide. But this could not be confirmed by later workers.

Shipp[24] obtained 2,2′,4,4′,6,6′-hexanitrostilbene (HNS) (XVII) in 30% yield by reacting 2,4,6-trinitrobenzyl chloride with alcoholic potassium hydroxide. The product melted at 316°, i.e. 105° above the melting point of the product obtained by Reich *et al.*[26]. It is likely that the product obtained by Reich *et al.*[24] was actually hexanitrodibenzyl (m.p., 213-15°). The correct structure of XVII (m.p., 316°) was established by following Shipp's unequivocal synthetic route[24] (Fig. 7).

Preparation by oxidation of nitro derivatives of toluene — A number of methods involving this approach have been developed. They can lead to derivatives of both dibenzyl and stilbene. Thus, Green *et al.*[27] obtained 4,4-dinitrodibenzyl (XVIII) (m.p., 180-182°C) by oxidising *p*-nitrotoluene with air in potassium hydroxide solution in methanol at room temperature. When the reaction mixture was warmed 4,4′-dinitrostilbene (XIX) resulted. Green and Baddiley[28] reacted 2,4-dinitrotolenue with diiodine in the presence of pyridine in potassium hydroxide solution in methanol at 40-50° and obtained 2,2′, 4,4′-tetranitrostilbene (XX) (m.p., 266-67°C) (Fig. 8).

Shipp and Kaplan[20] obtained 2,2′,4,4′,6,6′-hexanitrostilbene (HNS) (XVII) by oxidizing TNT with sodium hypochlorite. The method consists in adding 10 parts of 5% sodium hypochlorite solution to a chilled solution of 1 part of TNT in 10 parts of methanol. The solution is allowed to stand at ambient temperature until HNS precipitates as a fine crystalline product. The product is crystallized from nitrobenzene to yield pale yellow needles. The mechanism of the reaction is shown in Fig. 9.

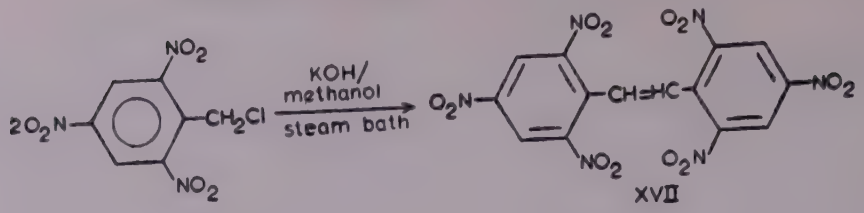
It is possible to isolate 2,4,6-trinitrobenzyl chloride (XXI) or the bimolecular product α-chloro-2,2′, 4,4′,6,6′-hexanitrodibenzyl (XXII) by 'short stopping' the reaction. This is indeed an excellent preparative reaction for the chloride (XXI), replacing the tedious series of reactions which had been the only known route for this compound[29].

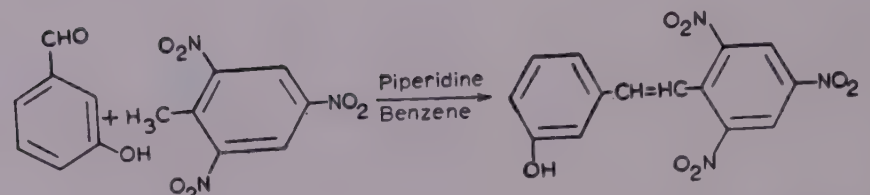
Nitro Derivatives of Aromatic Aza Pentalenes

Tetranitro derivatives of dibenzo-1, 3a,4, 6a-tetrazapentalene (TACOT) having two nitro group substituents in any position in each benzene ring are powerful explosives with unsual and outstanding high temperature stability properties[30]. TACOT, which is comparable to pentaerthythritol tetranitrate (PETN) in explosive power, has thermal stability greater than that reported for any known organic explosive compound or composition.

TACOT (XXIV) was described for the first time in 1960 in a patent[31] and later in many papers of Carboni *et al.*[32-37] in which the syntheses of this compound and its properties were reported. It can be obtained from *o*-phenylenediamine by the sequence of reactions shown in Fig. 10.

Tetranitrodibenzo-1, 3a, 4, 6a-tetraazapentalene (XXIV) is generally prepared from tetraazapentalene (XXIII) by direct nitration. The procedure[30] consists in adding 30 parts of fuming nitric acid to 1 part of dibenzo-1,3a,4,6a-tetraazapentalene in concentrated sulphuric acid. After 15 min, the mixture is heated to 60° and maintained at this temperature for an additional 15 min period. The orange mixture is poured into ice-water to yield TACOT, which can be recrystallized from dimethyl formamide. The product obtained is composed of numerous isomers of tetranitrodibenzo-1,3a,4,6a-tetraazapentalene, depending on





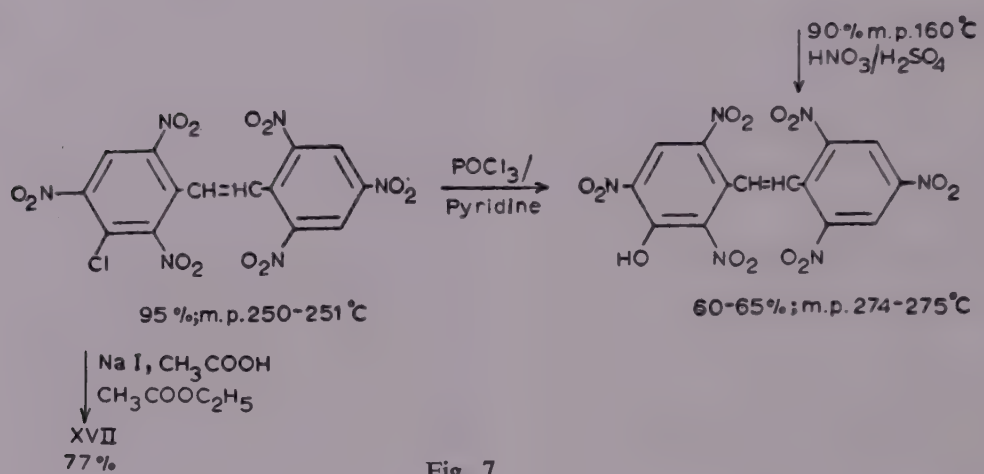


Fig. 7

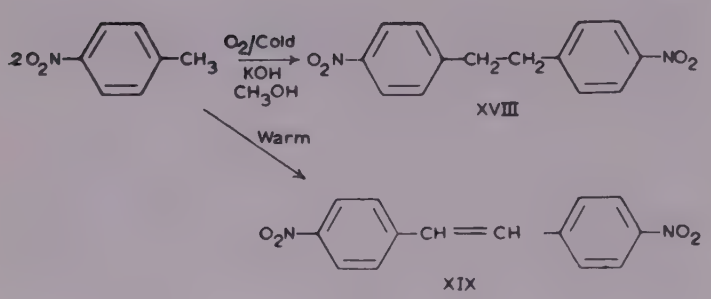


Fig. 8

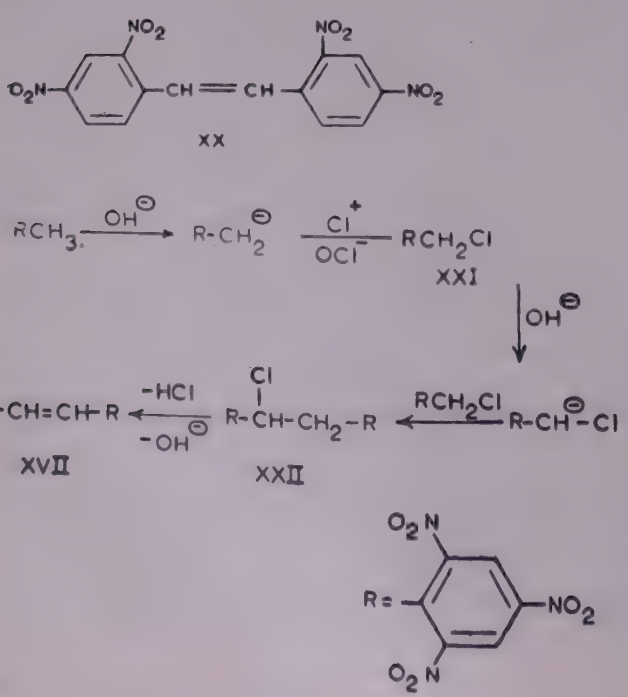


Fig. 9

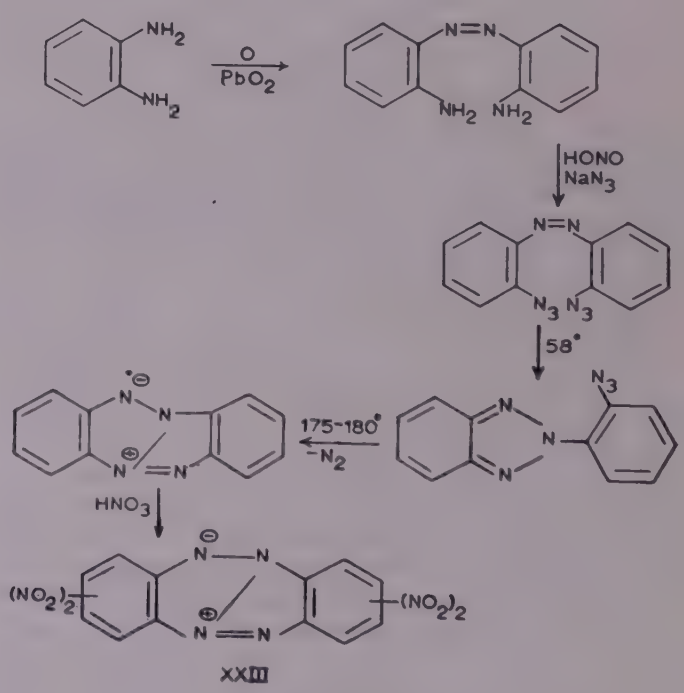


Fig. 10

the position of the nitro group (*ortho*, *meta* or *para*) in each individual benzene ring. But these isomers have been found to have similar explosive and thermal properties. Therefore, the product (TACOT), which is a mixture of the three isomers, is used as such in explosive compositions. Its ignition temperture (494°C) is the highest ever registered for explosives. Its explosive power is equal to 96% and 80-85% that of TNT and RDX respectively. It is highly insensitive to impact and compares favourably with dinitro-

benzene in this respect. Despite the insensitivity to impact and static charge, TACOT can be easily initiated by lead azide primer containing as little as 0·40 grains of lead azide.

Summary

The major synthetic approaches developed in recent years in the field of high temperature explosives (thermally stable, in sensitive to impact and capable of delivering large output of energy) are reviewed.

Acknowledgement

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New Horizons in Cyclopentanoid Syntheses*

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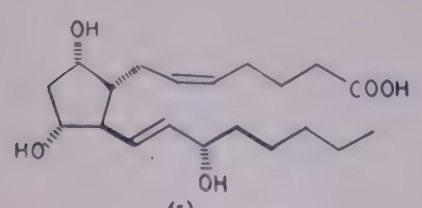
ALTHOUGH cyclopentanes have been known in chemical literature for over a century and in nature from times immemorial, interest in their syntheses and reactions has remained on a low key until recently. Strange as it may seem, this could be traced to the fact that till 1960, relatively few cyclopentanoids of reasonable complexity were known that could pose challenging problems to practising organic chemists. Further, the pre-eminent position of steroids and related natural products during the preceding few decades completely dominated the imagination of synthetic chemists and as a result the focus of their attention was the rapid and efficient acquisition of annulated cyclohexane rings[1]. However, recent discoveries and developments in the chemistry of natural and unnatural products have kindled the interest of synthetic organic chemists in the design of cylopentane ring systems and a flurry of activity has been witnessed[2–4] in this area during the past one decade.

Motivation for undertaking a synthetic venture is generally manifold. Mostly, it springs from the structural complexity and practical utility of the target molecule. In some cases, however, the mere urge to assemble frameworks endowed with either a novel architecture or some bizzare structural features gains ascendency over all other considerations. It is imperative that the great upsurge of interest in the synthesis of cyclopentanoids also owes its origin to some of these considerations. The two molecules that really set the ball rolling in this area were the prostanoids[5], e.g. prostaglandin $F_{2\alpha}$ (I), often referred to as the wonder drugs of 1980's and the supercyclopentanoid dodecahedrane (II). The synthetic challenge[6] associated with the construction of either I having stereospecific substitution on four contiguous carbon atoms and in all five chiral centres or II having a compact fusion of 12 five-membered rings, needs little testimony. Before considering the various synthetic strategies, it will be worthwhile to briefly survey the natural and unnatural cyclopentanoids of current interest. This exercise is essential to fully appreciate their structural versatility and practical utility in such diverse fields as perfumery and medicine.



(I)

(II)

*Based on a lecture delivered by the author at the 63rd Session of the Indian Science Congress at Bhubaneswar.

The structures of some of the more interesting cyclopentanoid natural products are depicted in Chart 1. Among them, *cis*-jasmone (III)[7] and *cis*-methyl jasmonate (IV) are two important perfumery materials currently favourite with the synthetic chemists. Some of the other natural products mentioned in Chart 1 include fungal metabolites, pentaleno lactone (V) and huristic acid (VI); marine natural products, capnellane (VII) and dolatriol (VIII); cytotoxic principles, plenolin (IX) and jatrrophone (X); monoterpenic glycoside genipin (XI) and loganin (XII); and the witch weed germination factor strigol (XIII).

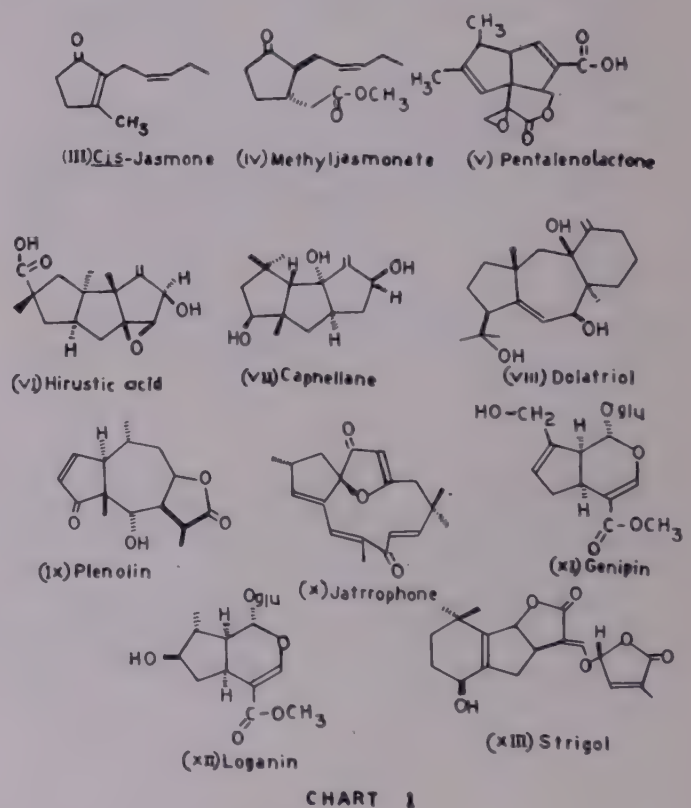


CHART 1

Some cyclopentanoid unnatural products (XIV-XXI), which are of synthetic interest due either to unusual strain factors or anticipated aromatic and antiaromatic character, or because of symmetry properties and similarity with familiar objects on a microscopic level, are depicted in Chart 2. Special mention must be made here of triquinacene (XV) and the bowl shaped molecule peristylane (XXI), which are considered as the logical precursors of dodecahedrane (II).

In the present article, we would not elaborate on the individual syntheses of compounds mentioned in Charts 1 and 2. The endeavour here will be to discuss, in a broader context, synthetic strategies of more recent vintage employed to assemble five-membered rings. We would, however, make frequent use of the

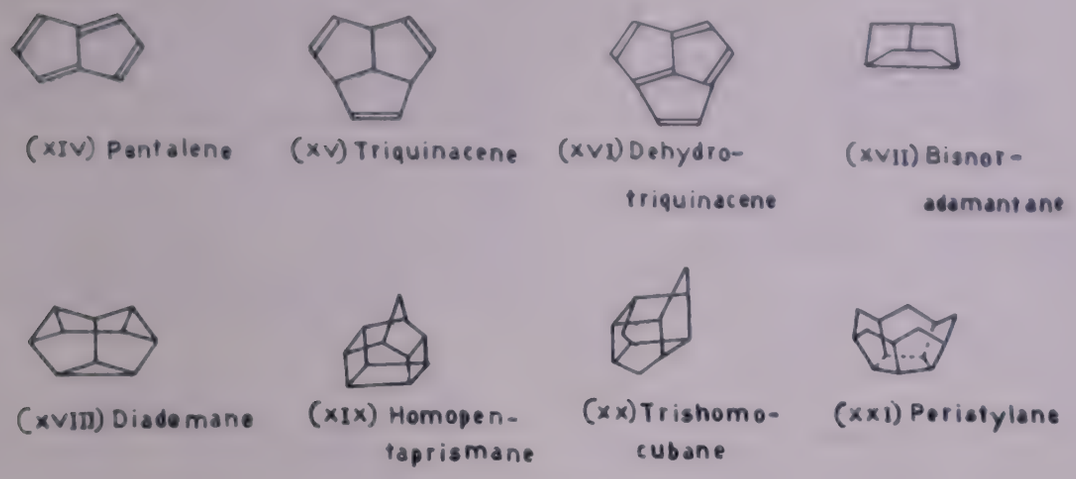
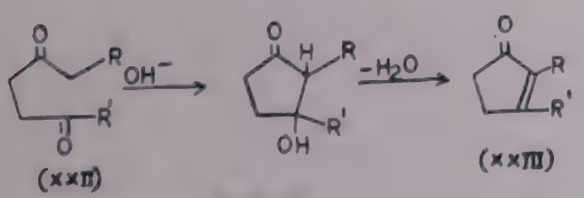


CHART 2

carbon skeleton of *cis*-jasmone (III)[7] to demonstrate the relative ease, merit and novelty of a particular approach. In fact, *cis*-jasmone (III) has turned out to be a testing ground for many new and imaginative efforts[2,3] in this area.

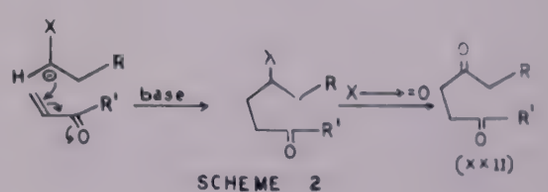
Cyclopentanoids via 1,4-Dicarbonyl System

Conceptually, one of the simplest approaches to the synthesis of cyclopentanoids and in particular to cyclopentenones (XXIII) is via the well known base catalyzed condensation of a suitable 1,4-dicarbonyl precursor (XXII) (Scheme 1). Although the aldol condensation of 1,4-dicarbonyl compounds to cyclopentenones is rather well established, the acquisition of 1,4-dicarbonyl system itself presents considerable practical difficulties. This is due to the highly labile nature of the 1,4-dicarbonyl system, which has too many reactive sites. Any fruitful route to the 1,4-dicarbonyl unit must, therefore, make effective use of the carbonyl protective groups and masked functional group equivalents[8] from which the requisite unit can be unmasked in a mild but efficient final step. In fact, it is the emergence of masked functionalities from its traditional protective role into the realm of electronic and regiospecific direction of activation, that has provided a new dimension[8] to the synthesis of the 1,4-dicarbonyl system.



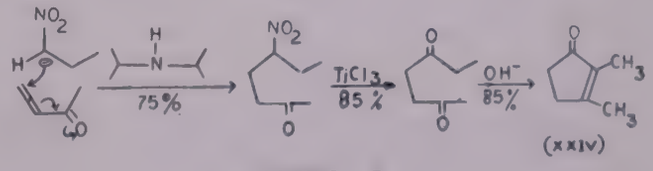
SCHEME 1

The most straightforward route to XXII is one that employs a nucleophilic acylation of an enone, i.e. 1,4-addition of a carbonyl anion equivalent to a suitable unsaturated acceptor. In the generalized presentation (Scheme 2), X must be a group capable of stabilizing a carbanion and which, after a 1,4-addition, can be readily transformed into a carbonyl.



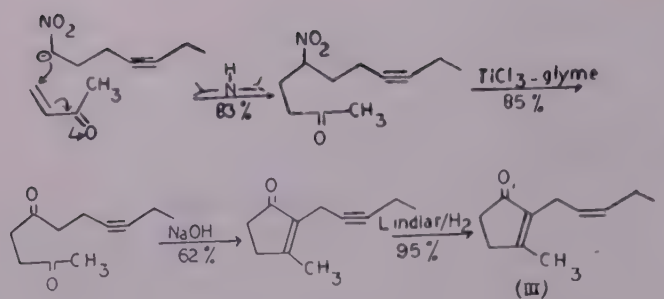
SCHEME 2

In other words, the group X serves as a latent carbonyl functionality. McMurry and Melton[9] and McMurry[10] utilized this concept employing the nitro group as the carbonyl group equivalent, as it readily forms a nitronate anion and can be converted through reduction with low valent titanium and hydrolysis to the 1,4-dicarbonyl precursor. The novelty of this procedure[9] lies in the superiority of Ti^{3+} reagent, over the traditional reagents, in carrying out the Nef reaction ($C\text{–}NO_2 \rightarrow C{=}O$). A synthesis of 2,3-dimethyl cyclopentenone (XXIV) from 1-nitropropane and methyl vinyl ketone (MVK) is depicted in Scheme 3. This scheme, which is both simple and versatile, has been adopted for a variety of cyclopentenone syntheses, including *cis*-jasmone (III) (Scheme 4).

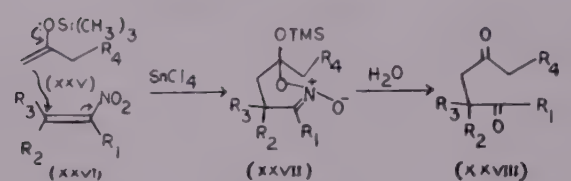


SCHEME 3

A related approach utilizing the nitro group as the ketone equivalent has been recently delineated by Yoshikoshi *et al.*[11] and is depicted in Scheme 5. Herein, trimethylsilyl enol ethers (OTMS), e.g. XXV, add in Michael fashion to α, β-unsaturated nitro-olefins (XXVI) in the presence of a Lewis acid catalyst like stannic chloride. Hydrolysis of the intermediate nitronic acid (XXVII) unravels the 1,4-dicarbonyl moiety (XXVIII). This synthetic sequence is essentially

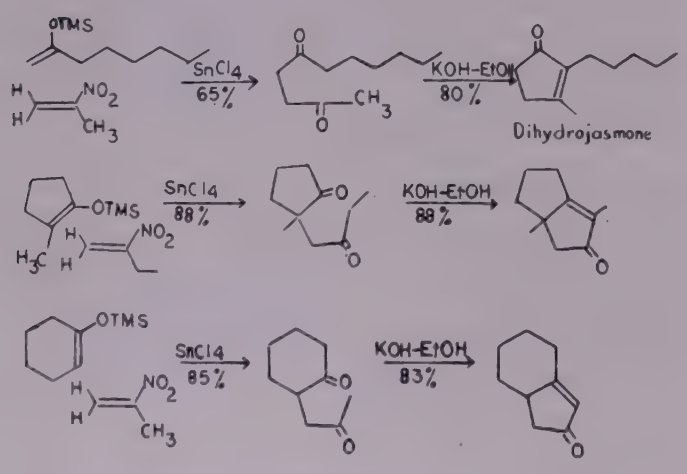


SCHEME 4



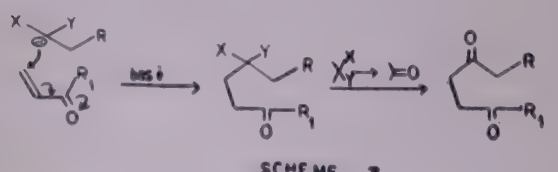
SCHEME 5

a one-pot operation and the yields are quite acceptable. The flexibility of this approach is evident from the ease with which the starting synthons [XXV from ketone — $(CH_3)_3$-SiCl-DMF and XXVI from nitroalkane-ketone base] are accessible. A few synthetic applications of the Yoshikoshi approach[11] to cyclopentenones, utilizing regiospecific enol ether formation, are shown in Scheme 6.



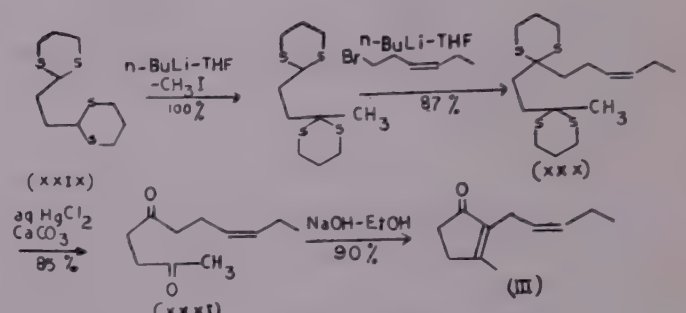
SCHEME 6

A logical variant of the functional group equivalence theme utilizes the grouping XY as the latent carbonyl eqivalent and the concept is depicted in Scheme 7 for assembling a 1,4-diketone unit. Dithianes, first introduced by Corey and Seebach[12] for the



SCHEME 7

direct alkylation of ketones, were among the first carbonyl anion equivalents of this type. An elegant cyclopentanoid synthesis has been designed[13] making optimum utilization of the dithiane alkylation procedure. The dithiane (XXIX) derived from succinaldehyde, on successive alkylation with methyl iodide and 1-bromo-*cis*-hex-3-ene, yielded XXX, which on removal of the mask furnished the desired precursor (XXXI) of *cis*-jasmone (III). The efficiency of the process can be gauged from the 61% overall yield of *cis*-jasmone (III) from XXIX (Scheme 8).

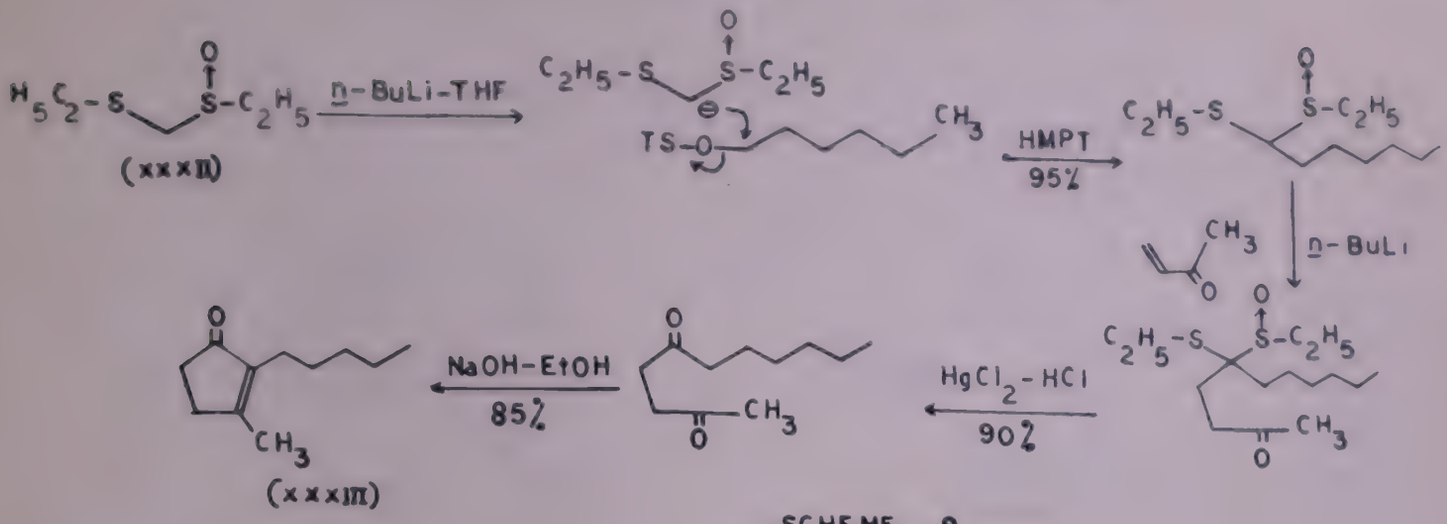


SCHEME 8

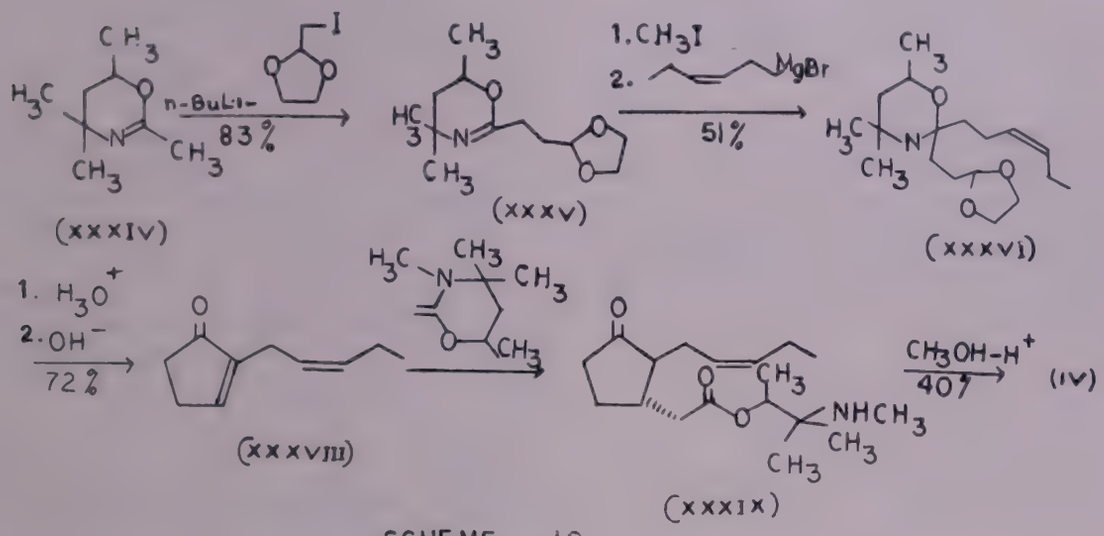
The enormous success of the dithiane alkylation method has stimulated several explorations of related systems. Schlessinger and coworkers[14,15], in a lucid series of communications, have described the synthesis of 1,4-dicarbonyl compounds employing ethyl thiomethylsulphoxide (XXXII, ETMS) as the carbonyl anion equivalent. The advantage of using ETMS lies in the fact that it readily forms a carbanion with bases and the mercaptal-S-oxide moiety can be readily hydrolysed, under mild conditions, to the corresponding carbonyl compounds in excellent yields. This scheme has been successfully implemented to develop excellent syntheses of *cis*-jasmone (III) and dihydrojasmone (XXXIII). The synthesis of the latter is depicted in Scheme 9.

Yet another route to 1,4-dicarbonyl compounds makes use of the dihydro-1,3-oxazine system[16] as the masked carbonyl anion equivalent. Moyer's synthesis[16] of *cis*-methyl jasmonate (IV) utilizing this approach is shown in Scheme 10. Alkylation of 2, 4,4, 6-tetramethyl-dihydro-1,3-oxazine (XXXIV) with 2-iodomethyl-1, 3-dioxolane produces XXXV, which on quaternization with methyl iodide *in situ* and reaction with the appropriate Grignard reagent furnishes XXXVI. Unmasking of the carbonyl group led to the production of the 1,4-dicarbonyl unit (XXXVII). Base catalyzed cyclization of XXXVII to 2-alkenyl-cyclopentenone (XXXVIII) and a novel 1,4-addition of acetic acid via XXXIX completed the synthesis of *cis*-methyl jasmonate (IV).

Certain stable and readily assembled cyclic systems also incorporate a latent 1,4-dicarbonyl unit, which can be unravelled in a simple one-step operation. Such systems include furan, substituted cyclopropanols and vicinal cyclobutanediols. For example, furans can conveniently[17-20] serve as the precursors of γ-diketones to which they are intimately related (Scheme 11). Taking advantage of this relationship,

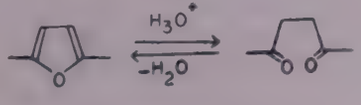


SCHEME 9



SCHEME 10

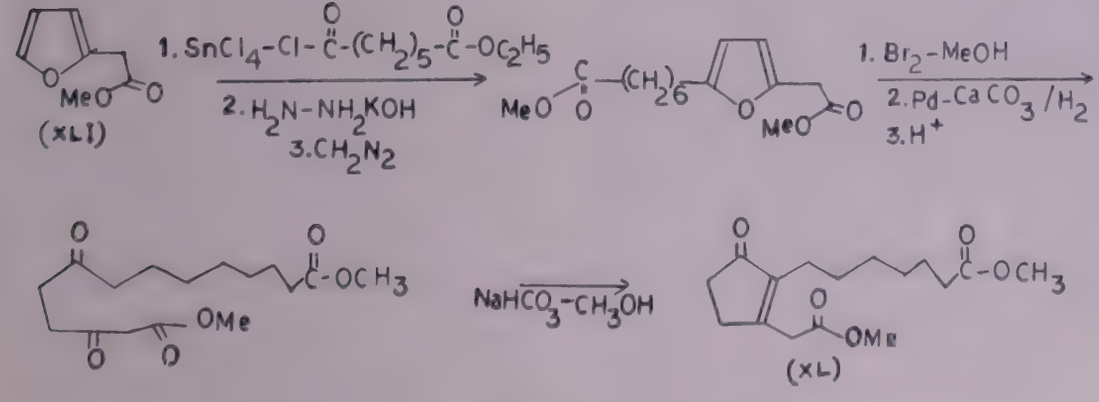
a classical but economical route to cyclopentenone (XL) from commercially available 2-furanyl acetate (XLI) has been developed (Scheme 12)[20]. The enone (XL) is of obvious interest in prostanoid synthesis.



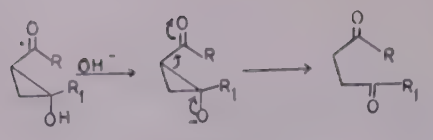
SCHEME 11

Wenkert *et al.*[21] and McMurry and Glass[22] made elegant use of cyclopropanol anions as 1,4-dicarbonyl precursors (Scheme 13). A simple route to *cis*-jasmone (III) has been developed utilizing this strategy (Scheme 14).

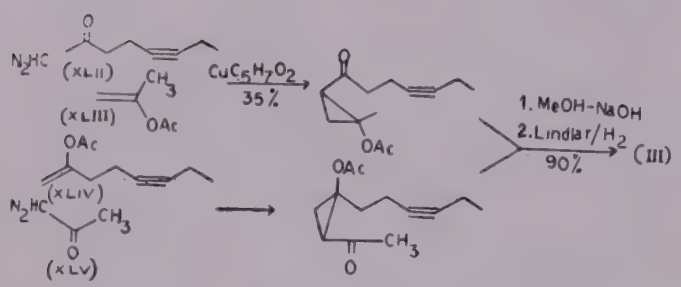
The cyclopropanol synthon is readily assembled through ketocarbenoid insertion into an enol acetate. The novelty of this carbenoid insertion reaction is that the functionality (enol acetate +α-ketocarbene) is interchangeable between the two reactants, i.e



SCHEME 12



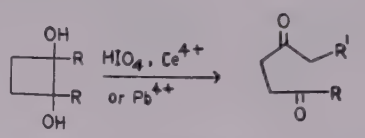
SCHEME 13



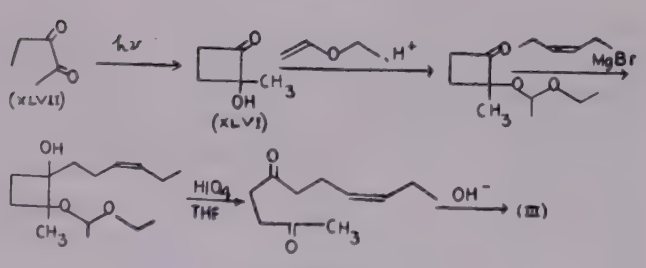
SCHEME 14

there is choice for acquiring the same 1,4-dicarbonyl unit either from XLII and XLIII or from XLIV and XLV.

Finally, vicinal cyclobutanediols can be readily cleaved by oxidising agents and serve as simple γ-diketone precursors (Scheme 15). Weinreb and Cvetovich[23] described a photochemical preparation of 1,2-cyclobutanediol (XLVI) from 2,3-pentanedione (XLVII) and cleaved it to the 1,4-dicarbonyl precursor of *cis*-jasmone (III). This approach is simple and efficient (Scheme 16).



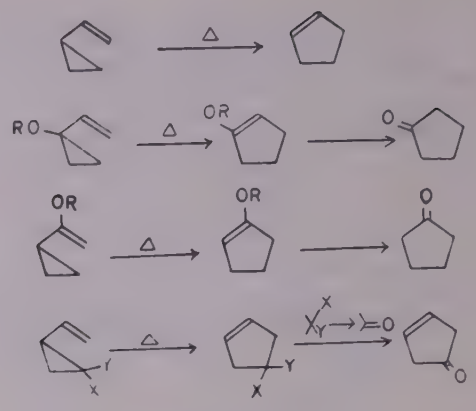
SCHEME 15



SCHEME 16

Cyclopentanoids via Cycloadditions

The thermal rearrangement of vinyl cyclopropanes offers a simple and convenient route to cyclopentenes (Scheme 17). A logical extension of this rearrangement to cyclopentanone synthesis would require the utilization of suitably functionalized vinyl cyclopropane derivatives possessing masked carbonyl groups. Thermolysis and unmasking could then provide a direct entry to cyclopentanoids. Several substituted vinyl cyclopropanes that can conceptually eventuate into cyclopentanones, on thermolysis followed by a gentle chemical transformation, are depicted in Scheme 17. The thermolysis route to cyclopentanones appears to be short, simple to manipulate and highly versatile. This route is particularly emenable to the synthesis of annulated cyclopentanoids.



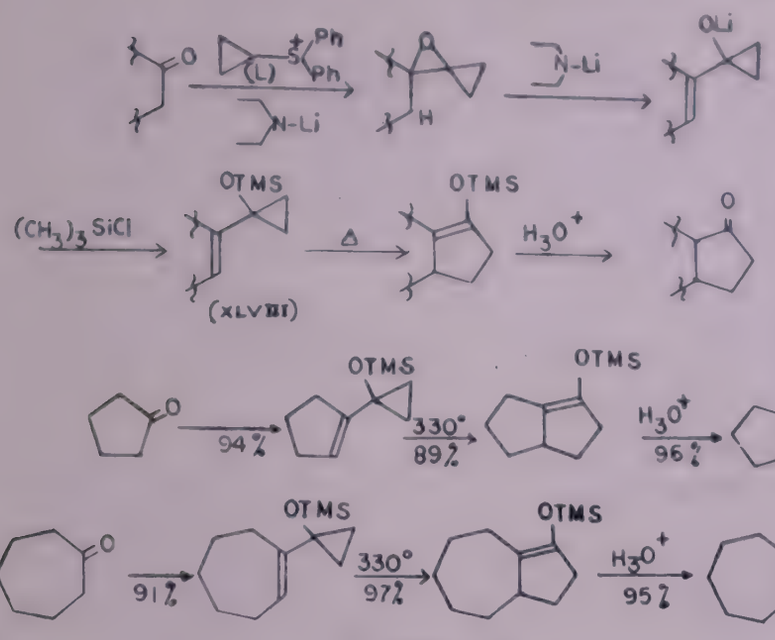
SCHEME 17

Trost *et al.*[24-26] outlined two very promising and general routes to cyclopentanones via the thermolysis of trimethyloxyvinyl cyclopropanes and phenylthiovinyl cyclopropanes and unravelling of the protected carbonyl group through mild, efficient procedures. Efficacious synthesis of precursor siloxyvinylcyclopropanes (XLVIII) and phenylthiovinylcyclopropanes (XLIX) were also developed by Trost *et al.*[24-26], utilizing two new synthons, diphenylsulphonium cyclopropylide (L)[24] and 1-lithiophenylcyclopropyl sulphide (LI)[26]. The two synthetic strategies with typical examples are summarized in Schemes 18 and 19. The yields reported by Trost are indeed remarkable and highlight the preparative value of the method.

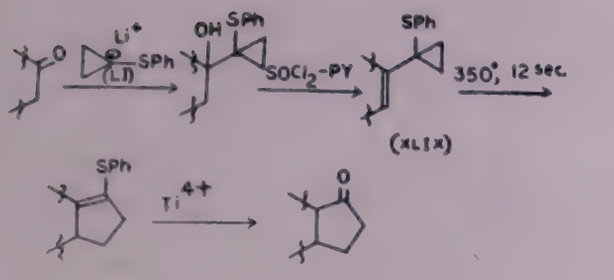
Another variant of the vinyl cyclopropane rearrangement depicted in Scheme 17 has been developed and exploited by Monti and coworkers[27]. Several examples of this route, involving thermal rearrangement of trimethylsilyl ethers of cyclopropyl ketones, are shown in Scheme 20. As cyclopropyl ketones can be obtained through well established synthetic procedures and simply converted to the trimethylsilyl enol ethers, this method too, like the previous one, is quite convenient.

Berkowitz and Ozorio[28,29] described the direct thermal reorganization of 3-cyclopropyl-3-oxo-propanoates (LII) to 2-cyclopentenones (L-III). The method appears to be fairly general, although the yields vary significantly with the thermolysis conditions. A synthesis of *cis*-jasmone (III) in 29-32% overall yield from readily obtainable starting synthon has been reported (Scheme 21). Finally, a direct route[30] to cyclopentenone (LIV) via the thermolysis of dithiane derivative of vinylcyclopropanone (LV) has been described (Scheme 22).

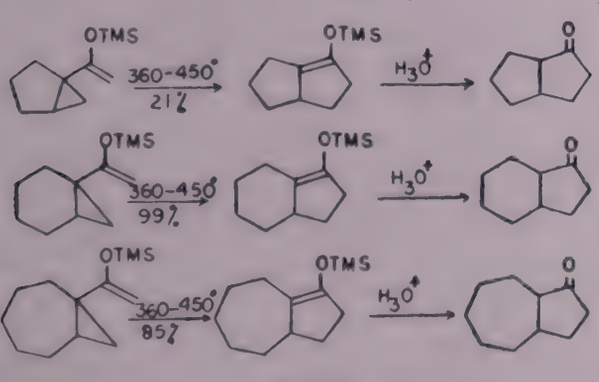
The known propensity of cyclopropanone to undergo 1,3-dipolar cycloadditions with electron rich olefins and dienes has been fruitfully exploited by Noyori *et al.*[31,32] to develop a new cyclopentenone synthesis. Thus, reaction of α, α'-dibromoketones with enamines in the presence of diiron-nonacarbonyl furnished cyclopentenones in one step in 50-100% yield. For example, reaction of LVI with α-morpholinostyrene (LVII) with $Fe_2(CO)_9$ reducing agent gave the cyclopentenone (LVIII) in 94% yield



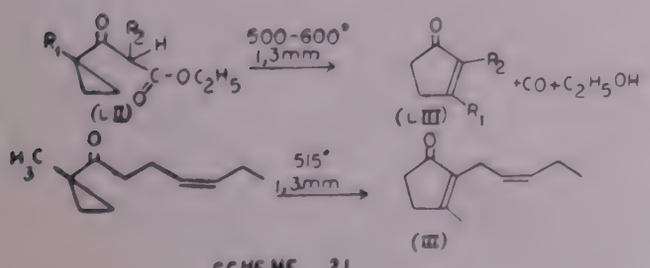
SCHEME 18



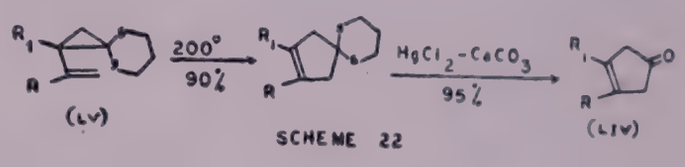
SCHEME 19



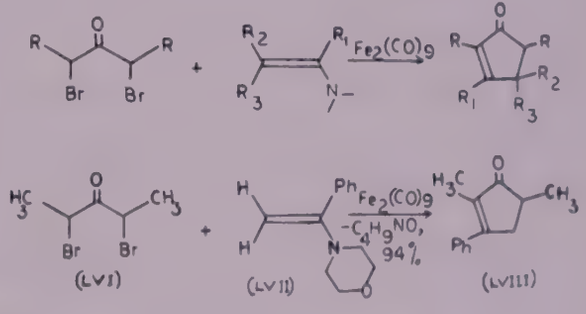
SCHEME 20



SCHEME 21



SCHEME 22



SCHEME 23

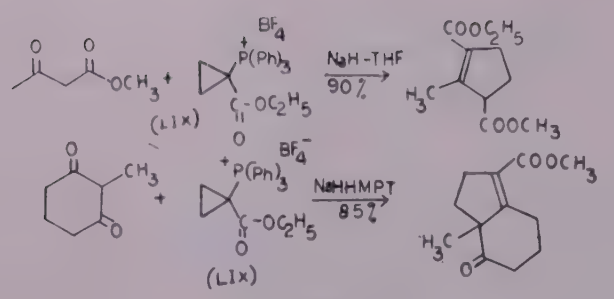
(Scheme 23). The molecule of morpholine is eliminated under the reaction conditions.

Another novel route to cyclopentenes developed[33] using carboethoxy-cyclopropyltriphenyl phosphoniumtetrafluroborate is presented in Scheme 24.

Lastly, several routes involving ring contraction of suitably functionalized six-membered rings have been devised[34,35] for generating a variety of five-membered rings. However, due to their limited preparative value and scope, these will not be detailed here.

Synthesis of Polyfused Cyclopentanoids

So far we have mainly dwelt upon some of the general approaches to cyclopentanoids of natural occurrence. We now turn our attention to some specific strategies that have been evolved recently for the rapid acquisition of condensed, polyfused cyclopentanoids. The impetus for these endeavours was provided by dodecahedrane (II) and its two most logical precursors,

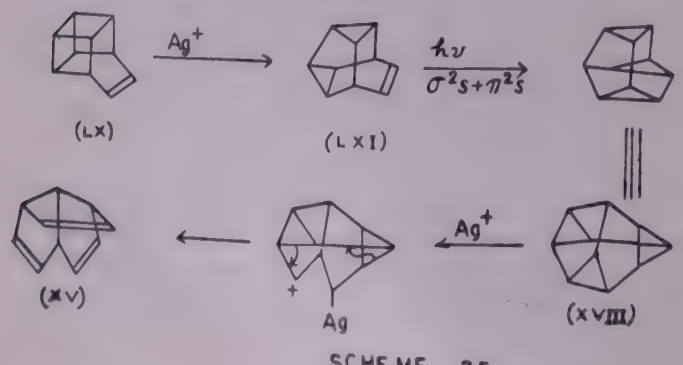


SCHEME 24

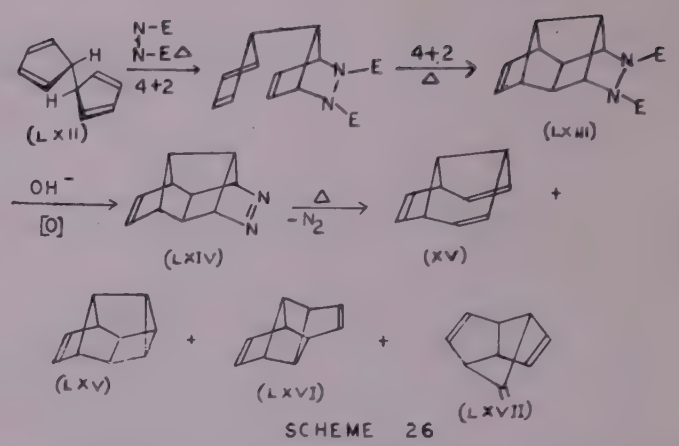
triquinacene (XV)[36] and peristylane (XXI)[37]. Dodecahedrane (II) holds this pre-eminent position because of the presence of 12-polyfused rings generating the highest known point group symmetry (Ih) and the existence of a cavity of 2.0-2.5 Å diameter completely enclosed within the carbon framework. Interest in triquinacene (XV) resides in its predicted behaviour as a precursor for more exotic structures. For example, introduction of an additional double bond in it could provide the higher homologue (XVI) of pentalene. More interestingly, if the two molecules of XV could be made to adopt correct stance for dimerization, it could provide a most striking synthesis of the $(CH)_{20}$ polyhedron (II).

Triquinacene (XV), in its own right, presents an interesting exercise in assembling five-membered rings. An elegant but arduous multistep preparation of XV was reported by Woodward *et al.*[36]. Recently, two fascinating approaches to triquinacene (XV), representing outstanding feats of molecular acrobatics, have been reported by de Meijere and coworkers[38,39] and Wyvratt and Paquette[40]. The starting material of de Meijere synthesis is basketene (LX), a bishomocubane derivative prepared from cyclooctatetraene in a multistep sequence. The transformation of basketene (LX) to XV through the intermediacy of snoutene (LXI) and diademane (XVIII) is depicted in Scheme 25 and represents a veritable example of $(CH)_{10}$ molecular reorganisations.

The Paquette route[41] to triquinacene (XV) is presented in Scheme 26. The key to this brilliant synthesis is a combination of inter- and intra-molecular 4+2 cycloadditions (Domino Diels-Alder reactions) to 9,10-dihydrofulvalene (LXII). Hydrolysis and oxidation of the resulting adduct (LXIII) furnishes the azo compound (LXIV) in good yield. Photolysis of



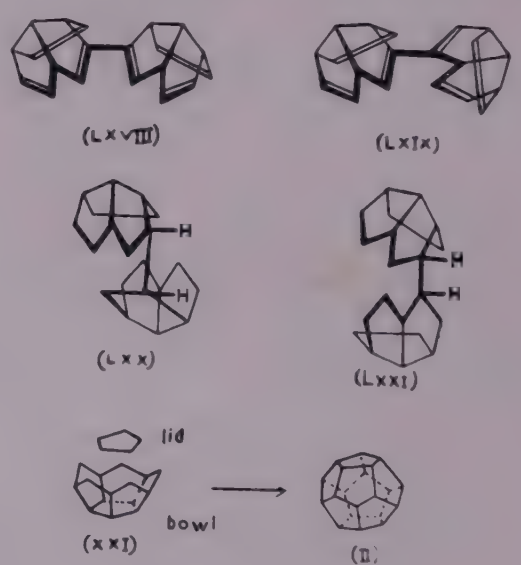
SCHEME 25



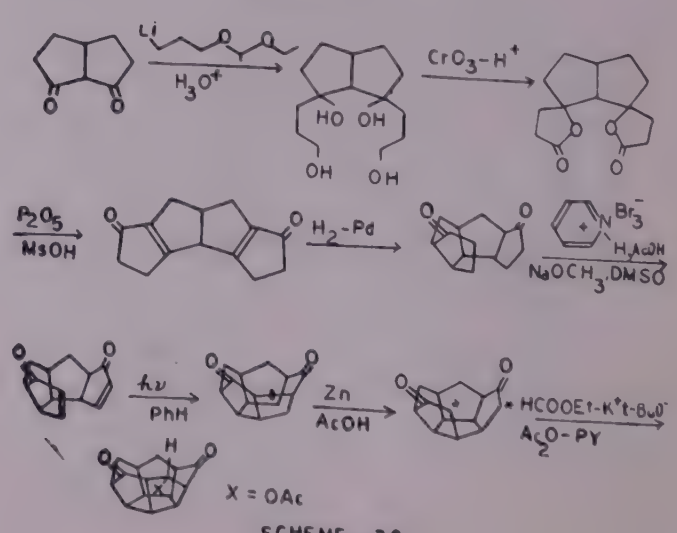
SCHEME 26

LXIV yielded four novel hydrocarbons [XV, LXV, LXVI and LXVII], among which triquinacene (XV) was the major product formed in 60% yield. This route is, therefore, of preparative value and renders available XV in quantities sufficient for further chemical explorations.

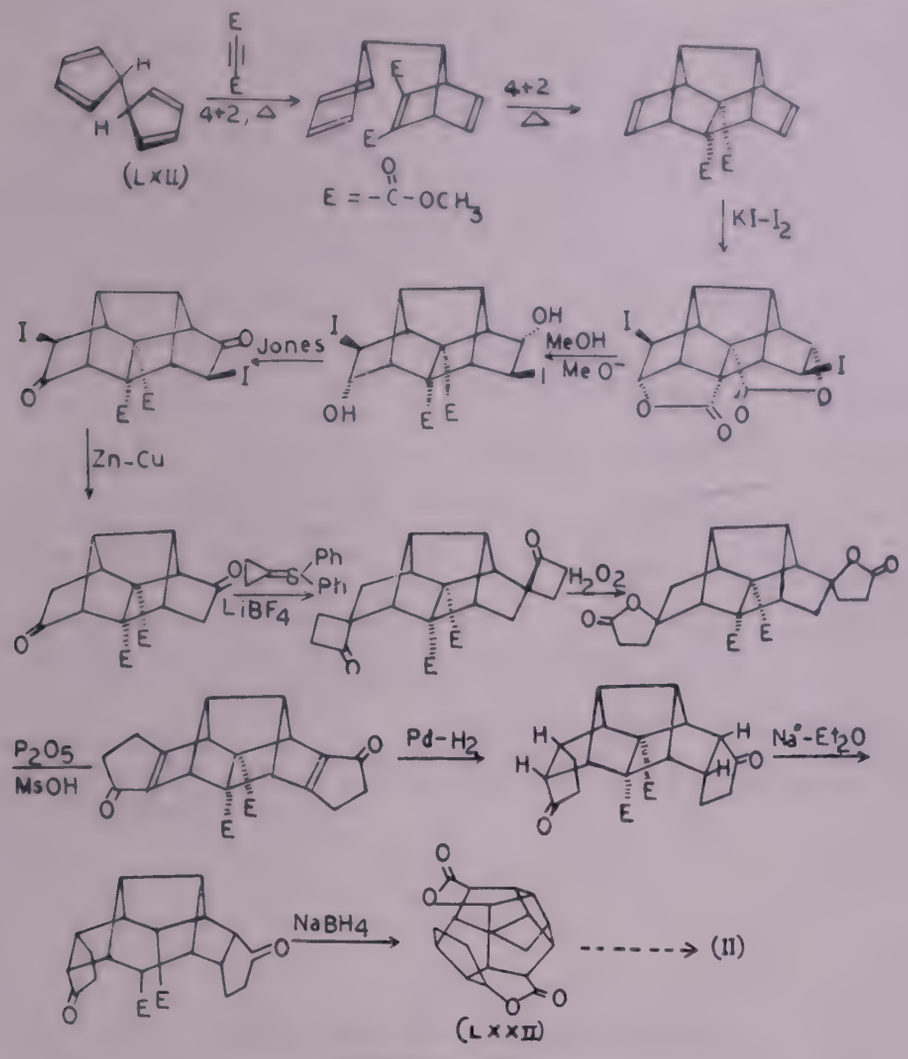
Although several attempts to dimerize triquinacene (XV) to dodecahedrane (II) in proper orientation have proved abortive, a few dimeric *meso* (LXVIII) and *dl*-bistriquinacenes (LXIX) as well as distereoisomeric bivalvanes (LXX, LXXI) have been reported[41].



SCHEME 27



SCHEME 28



SCHEME 29

Eaton considered the dodecahedrane problem from another perspective and pinned his faith in a novel and aesthetically pleasing, 'bowl' and 'lid' approach depicted in Scheme 27. His synthesis of the 'bowl', appropriately termed peritylane (XXI), represents a simple and effective way of building a network of five-membered rings (Scheme 28)[37].

Finally, Paquette *et al.*[42,43] has ingeniously coupled the 'Domino Diels-Alder' approach with Eatons' strategy to synthesize a trisecododecahedrane derivative (LXXII), as detailed in Scheme 29. This is the closest organic chemists have reached to their most prized and sought after molecule (II). Thus, the quest for II goes on unabated.

Summary

Some of the new synthetic strategies and designs directed towards complex cyclopentanoids are highlighted. Taking *cis*-jasmone and dodecahedrane as representative examples from the area of natural and unnatural product chemistry respectively, various synthetic approaches to these and related compounds have been discussed.

Acknowledgement

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Photochemistry of Flavonoids

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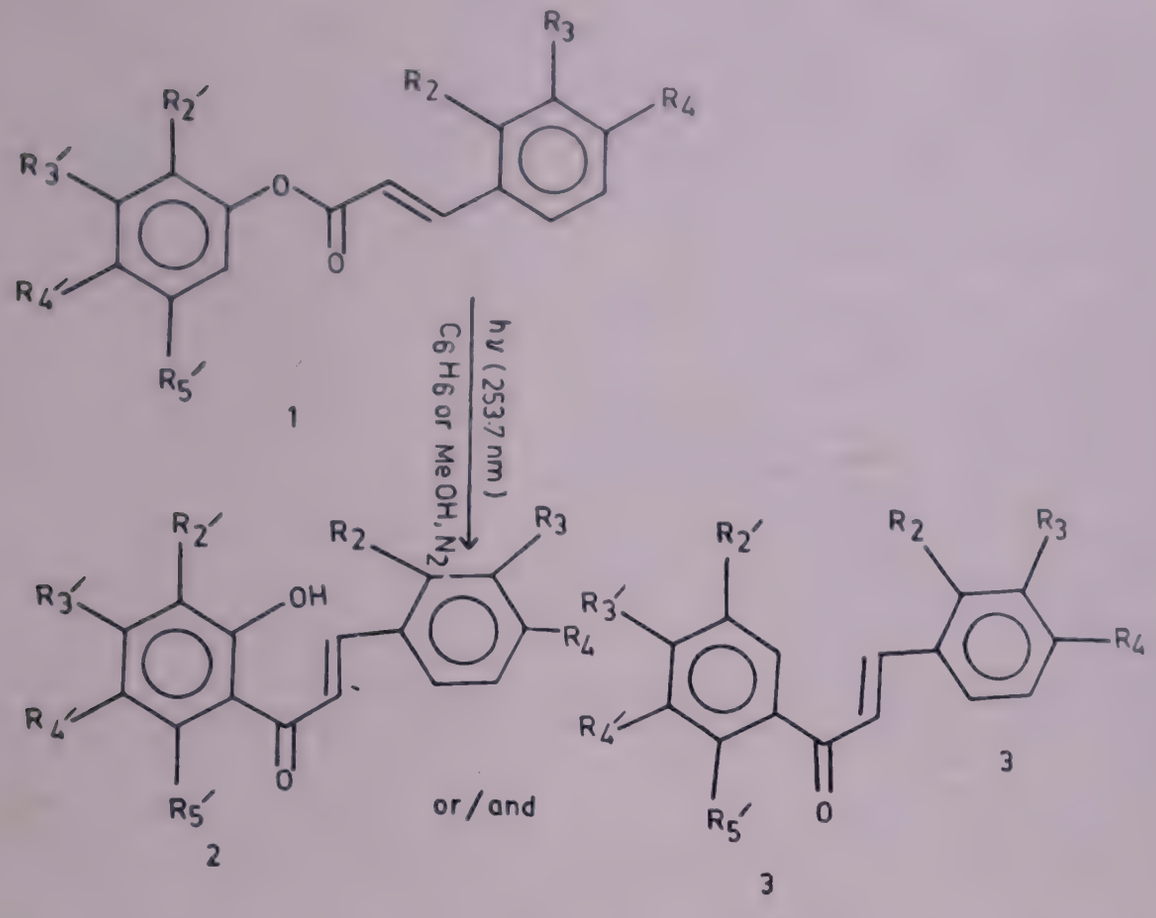
ORGANIC photochemistry is of considerable importance, because it has revealed new types of organic reactions and provided valuable syntheses of organic compounds, including natural products, which are otherwise difficult to obtain. Interest in this field has been growing since 1964, when the first International School was arranged at Strasbourgh[1]. This is reflected in the publication of a large number of books[2-22], and series volumes[23-26]. Oxidation with singlet oxygen is a comparatively recent development and is found to take place in many biochemical processes, such as dye-sensitized photo-oxidations (photodynamic action), certain blood diseases, cancer-inducing mechanisms, ageing mechanism, bactericidal activity of phagocytes and metabolic hydroxylations[27].

Flavonoids which constitute an important group of natural products have been studied photochemically much less than other groups of compounds like steroids. The information available on the photochemical behaviour of flavonoids is scattered over a large number of research papers. The present article attempts to review the major recent developments.

Photo-Fries Rearrangement of Phenyl Cinnamates and Synthesis of 2′-Hydroxychalcones

A large number of 2′-hydroxychalcones (**2**) occur in nature[28,29]. The possibility of getting them by photo-Fries rearrangement of phenyl cinnamates was first studied by Obara *et al.*[30,31], who isolated two compounds, 2′-hydroxychalcone (**2a**) and 4′-hydroxychalcone (**3c**) in 10% and 20% yields respectively by irradiating unsubstituted phenyl cinnamate (**1a**)[30]. Both the chalcones were *trans* and the *cis* isomer could not be isolated. In a parallel series of experiments with *p*-tolylcinnamate and phenyl-*p*-methoxycinnamate, 5′-methyl-2′-hydroxychalcone and 4-methoxy-2′-hydroxychalcone[30] were obtained. However, photo-irradiation of 2,3- and 3,5-dihydroxyphenyl cinnamates could not give pure trihydroxychalcones[32]. These studies were extended by Ramakrishnan and Kagan[33] to synthesize such 2′-hydroxychalcones as have oxygenation patterns similar to those of the common natural flavonoids. They studied the photo-Fries rearrangement of a number of phenyl cinnamates having different oxygenation patterns in two benzene rings and used methoxymethylation technique of protecting free hydroxyls



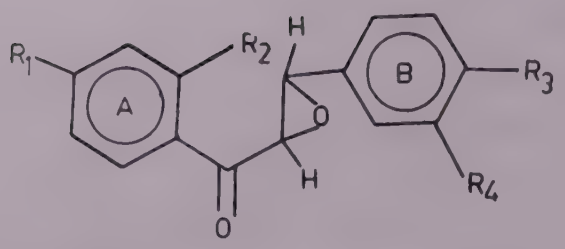
For 1-3 :

a) $R_2' = R_3' = R_4' = R_5' = R_2 = R_3 = R_4 = H$
b) $R_2' = OMe$; $R_3' = R_4' = R_5' = R_2 = R_3 = R_4 = H$
c) $R_3' = OH$; $R_2' = R_4' = R_5' = R_2 = R_3 = R_4 = H$
d) $R_3' = R_5' = OH$; $R_2' = R_4' = R_2 = R_3 = R_4 = H$
e) $R_3' = R_5' = R_2 = OH$; $R_2' = R_4' = R_3 = R_4 = H$
f) $R_3' = R_5' = R_4 = OH$; $R_2' = R_4' = R_2 = R_3 = H$
g) $R_3' = R_5' = OH$; $R_4 = OMe$; $R_2' = R_4' = R_2 = R_3 = H$
h) $R_3' = R_5' = R_3 = R_4 = OH$; $R_2' = R_4' = R_2 = H$
i) $R_3' = R_5' = R_4 = OH$; $R_3 = OMe$: $R_2' = R_4' = R_2 = H$
j) $R_3' = R_5' = OH$; $R_3 = R_4 = OMe$; $R_2 = R_4' = R_2' = H$
k) $R_3' = OH$; $R_5' = OMe$; $R_2' = R_4' = R_2 = R_3 = R_4 = H$
l) $R_5' = OH$; $R_3' = OMe$; $R_2' = R_4' = R_2 = R_3 = R_4 = H$
m) $R_2' = R_4' = R_2 = R_3 = R_4 = H$; $R_3' = OH$; $R_5' = OMe$
n) $R_2' = R_3' = O\text{-}CH_2\text{-}O\text{-}CH_3$; $R_4' = R_5' = R_2 = R_3 = R_4 = H$
p) $R_2' = R_4' = O\text{-}CH_2\text{-}O\text{-}CH_3$; $R_3' = R_5' = R_2 = R_3 = R_4 = H$
q) $R_3' = R_5' = O\text{-}CH_2\text{-}O\text{-}CH_3$; $R_2' = R_4' = R_2 = R_3 = R_4 = H$
r) $R_2' = R_3' = OH$; $R_4' = R_5' = R_2 = R_3 = R_4 = H$
s) $R_2' = R_4' = OH$; $R_3' = R_5' = R_2 = R_3 = R_4 = H$
t) $R_3' = R_5' = OH$; $R_2 = R_4' = R_2 = R_3 = R_4 = H$

in cinnamoyl chlorides during esterification. 2-Methoxyphenyl cinnamate (**1b**) and 3-hydroxyphenyl cinnamate (**1c**) were found to yield products of only *ortho* migration, viz. (**2b**) and (**2c**) respectively. Similarly, monoesters (**1d-j**) of phloroglucinol and hydroxycinnamic acids, when photolyzed in benzene or methanol, gave only one product, because the products of *ortho* and *para* migration are identical. Various 2′,4′,6′-trihyroxychalcones (**2d-j**) having different oxygenation patterns in the ring B were prepared by this method. It was, therefore, concluded that the photo-Fries rearrangement can be successfully used for the synthesis of polyhydroxychalcones, which could be subsequently converted into flavanones. It may be emphasized that in contrast to the acid-catalyzed acylation reactions, isomerization of the initially formed chalcones into flavanones does not occur immediately in photochemical reactions.

Bhatia and Kagan[34] prepared the monocinnamate (**1k**) of phloroglucinol monomethyl ether and by its photorearrangement in methanol, obtained two products, viz. 2′,6′-dihydroxy-4′-methoxychalcone (**2l**) and 2,4′-dihydroxy-6′-methoxychalcone (**2m**) which were characterized on the basis of NMR spectra. It was concluded that the chalcone isolated from *Lindera umbellata*[35], *Pinus clausa*[36] and the fern *Pityrogramma chrysophylla*[37] has the structure (**2l**).

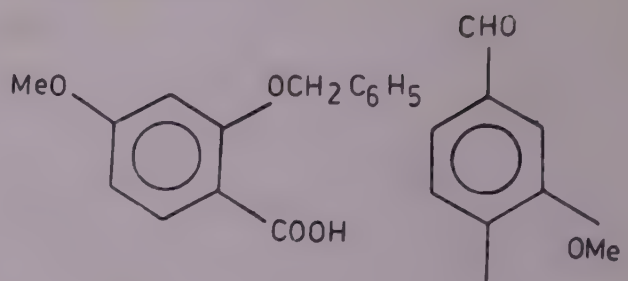
Recently, Onodera and Obara[38] photolyzed 2,3-; 2,4-; and 3,5-bis(methoxymethoxy)phenylcinnamates (**1n**, **1p** and **1q** respectively) in benzene and obtained 2′-hydroxy-3,′4′-; 2′-hydroxy-3′,5′-; and 2′-hydroxy-4′,6′- bis(methoxymethoxy)chalcones (**2n**, **2p** and **2q** respectively) in 6-7 % yields. These chalcones, on heating with methanolic HCl, afforded 2′,3′,4′-; 2′,3′,5′-; and 2′,4′,6′-trihydroxychalcones (**2r**, **2s** and **2t** respectively).



4 $R_1 = R_3 = R_4 = OMe$, $R_2 = O.CH_2.C_6H_5$

5 $R_1 = R_2 = OMe$, $R_3 = R_4 = H$

6 $R_1 = R_2 = R_3 = R_4 = OMe$



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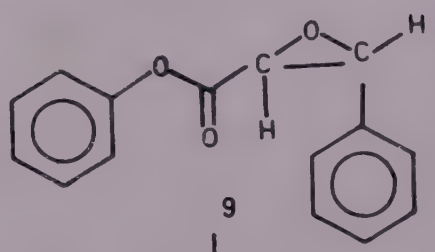

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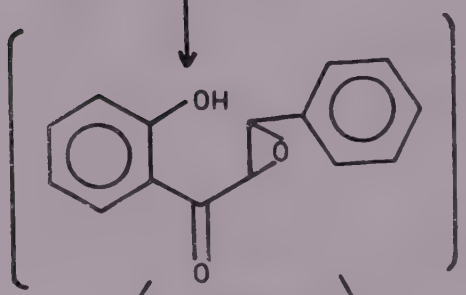
hυ (253·7 nm) C_6H_6, N_2



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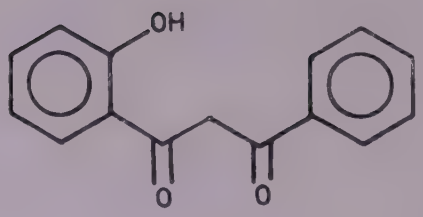

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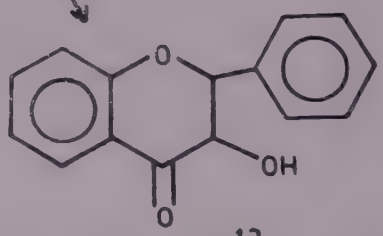

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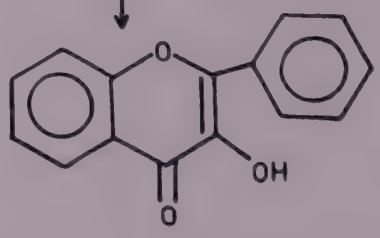

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The protection of hydroxyl groups of dihydroxyphenylcinnamates with methoxymethyl group can thus be used for obtaining trihydroxychalcones by photo-Fries rearrangement.

Photoconversion of 2′-Hydroxychalcones into Flavanones and Flavonols

The possibility of the production of flavanone (yield, 53%)[39] on irradiating 2′-hydroxychalcone in benzene provided an alternative method of getting flavanones and related compounds through the agency of light. However, 2′-hydroxy-α-methoxy-*trans*-chalcones on irradiation at 350 nm got converted into the corresponding *cis*-chalcones[40]. The recent conversion of 2′,4′6′-trihydroxychalcone into galangin by photosensitized oxidation in the presence of air

using catalytic amount of methylene blue[41] indicated the possibility that chalcones get directly converted into flavonols in plants.

Photolysis of simple unsubstituted chalcone epoxide — Bodforss[42] was the first to photolyze an unsubstituted chalcone epoxide in 1918. He isolated its rearranged product, 1,3-dibenzoylmethane. This photoisomerization may be explained in two consecutive steps: (i) fission of the $C_{(\alpha)}-O$ bond of the oxide ring, and (ii) subsequent 1,2-shift of the β-hydrogen to the α-position. Contrary to the first step in the photoreaction, thermal, acid or base catalyzed isomerization of α,β-epoxyketones proceeds generally via fission of the $C_{(\beta)}$—O bond of the oxide ring.

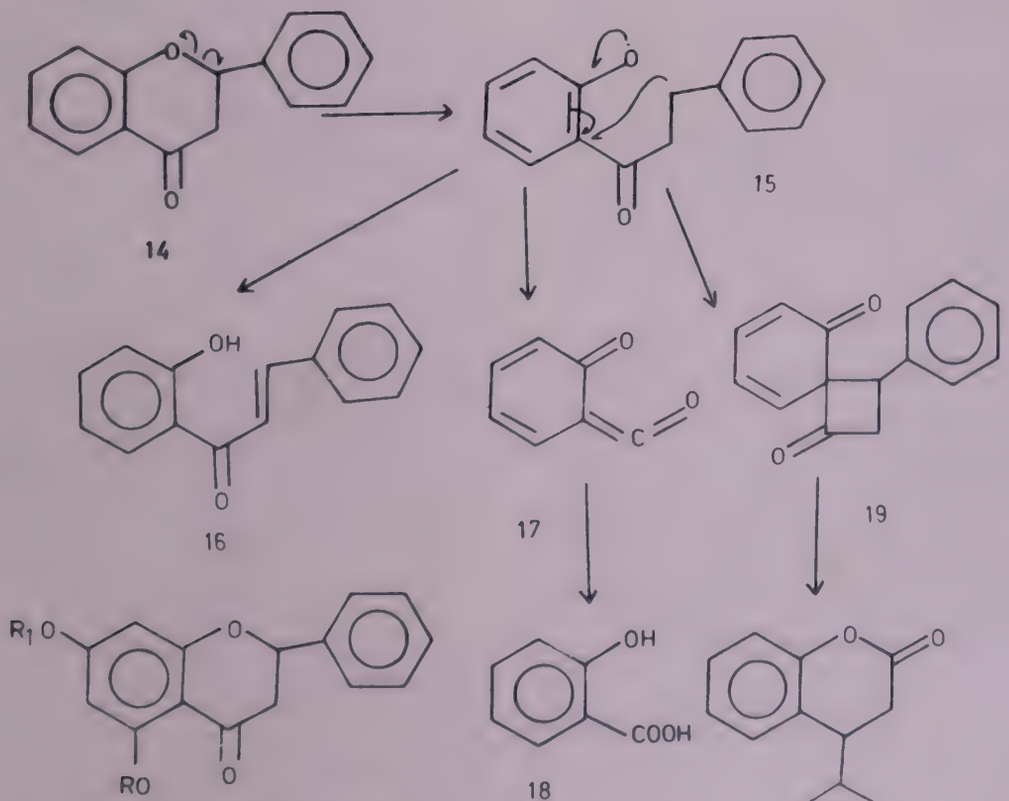
Photolysis of 2′-alkoxychalcone epoxides — Parthasarthy and Sharma[43] irradiated the following 2′-alkoxy chalcone epoxides in methanol in the presence of air: (a) 2′-benzyloxy-3,4,4′-trimethoxy- (**4**); (b) 2′,4′-dimethoxy- (**5**); and (c) 2′,4′,3,4-tetramethoxy- (**6**) chalcone epoxides. In each case the benzoic acid derivative corresponding to ring-A and the benzaldehyde derivative corresponding to ring-B were formed. For example, **4** gave 2-benzyloxy-4-methoxybenzoic acid (**7**) and veratraldehyde (**8**). However, according to Gupta[43], when trimethoxychalcone epoxide was irradiated in methanol in the presence of nitrogen, two crystalline products isolated were: 4,2′,4′-trimethoxydibenzoylmethane and a compound having dihydroisobenzofuran structure. This difference in the results of Gupta[44] and Parthasarthy *et al.*[43] is obviously due to the differences in the light absorbed and atmosphere provided.

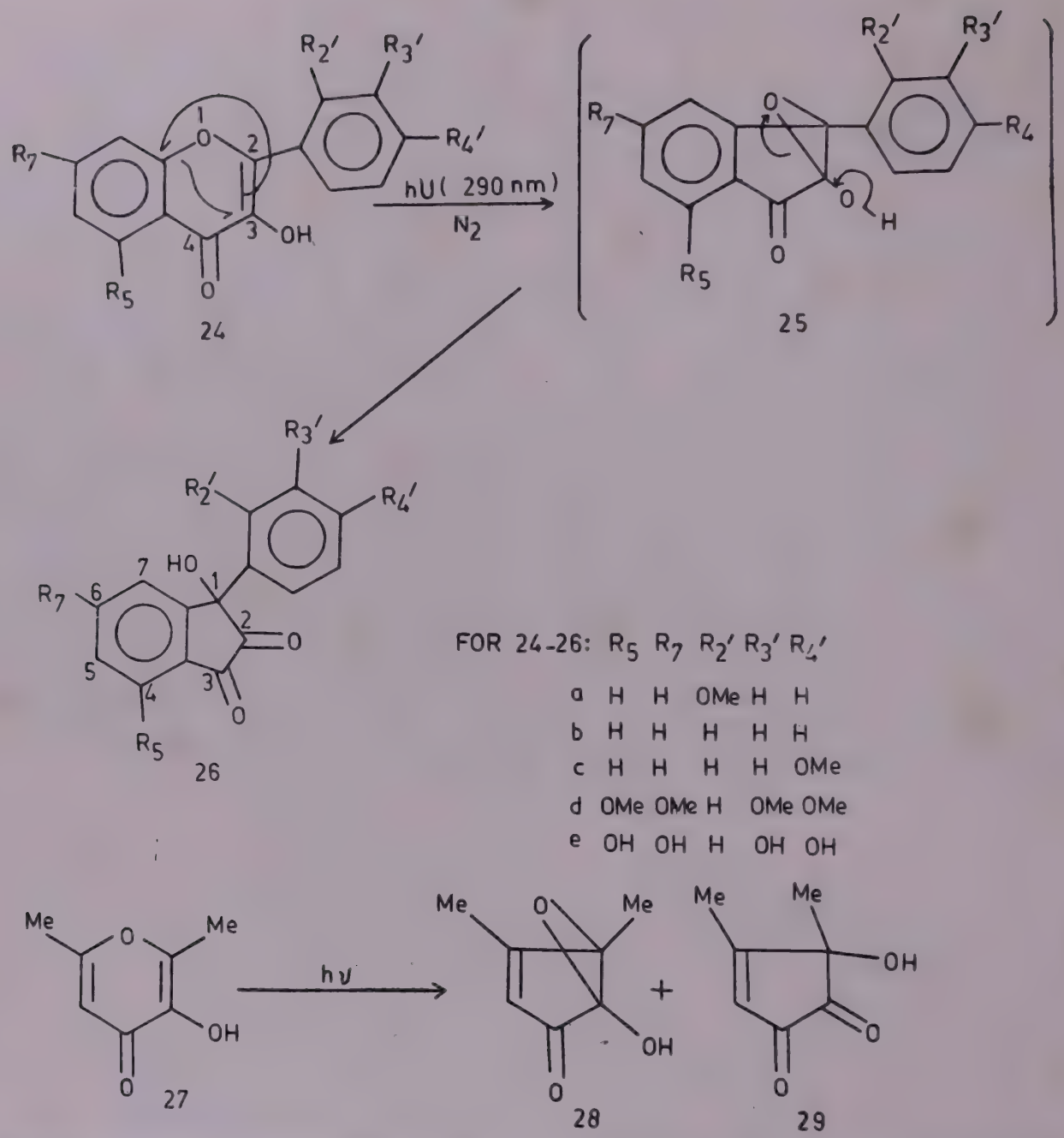
Unsubstituted phenylepoxycinnamate (**9**) was irradiated in nitrogen atmosphere by Ramakrishnan and Kagan[45]. The isolation of *o*-hydroxy-ω-benzoylacetophenone (**11**), 3-hydroxyflavanone (**12**) and flavonol (**13**) as some of the products has been explained on the basis of the formation of 2′-hydroxyepoxychalcone (**10**) as an intermediate compound.

Photochemistry of Flavanones

On irradiating unsubstituted flavanone (**14**) in benzene, Mack and Pinhey[46] isolated the following three products: (i) 2′-hydroxychalcone (**16**) (20%), (ii) 4-phenyl dihydrocoumarin (**20**) (13%), and (iii) salicylic acid (**18**) (4·1%). The initial product of photolysis was believed to be a diradical (**15**) in analogy with the behaviour of the simple aryl ethers[47,48] Intramolecular hydrogen abstraction then led to 2′-hydroxychalcone (**16**), while fragmentation gave ketoketene (**17**) which reacted with water to yield salicylic acid (**18**). Similarly, the biradical (**15**) afforded the intermediate (**19**) which underwent further photo-rearrangement to dihydrocoumarin (**20**).

Alpinetin (**21**), pinocembrin (**22**) and pinostrobin (**23**) were irradiated by Matsuura *et al.*[49] and found to be unaffected. This suggests that flavanones having chelated hydroxyl group and phenolic group in position 7 remain unaffected during photolysis.



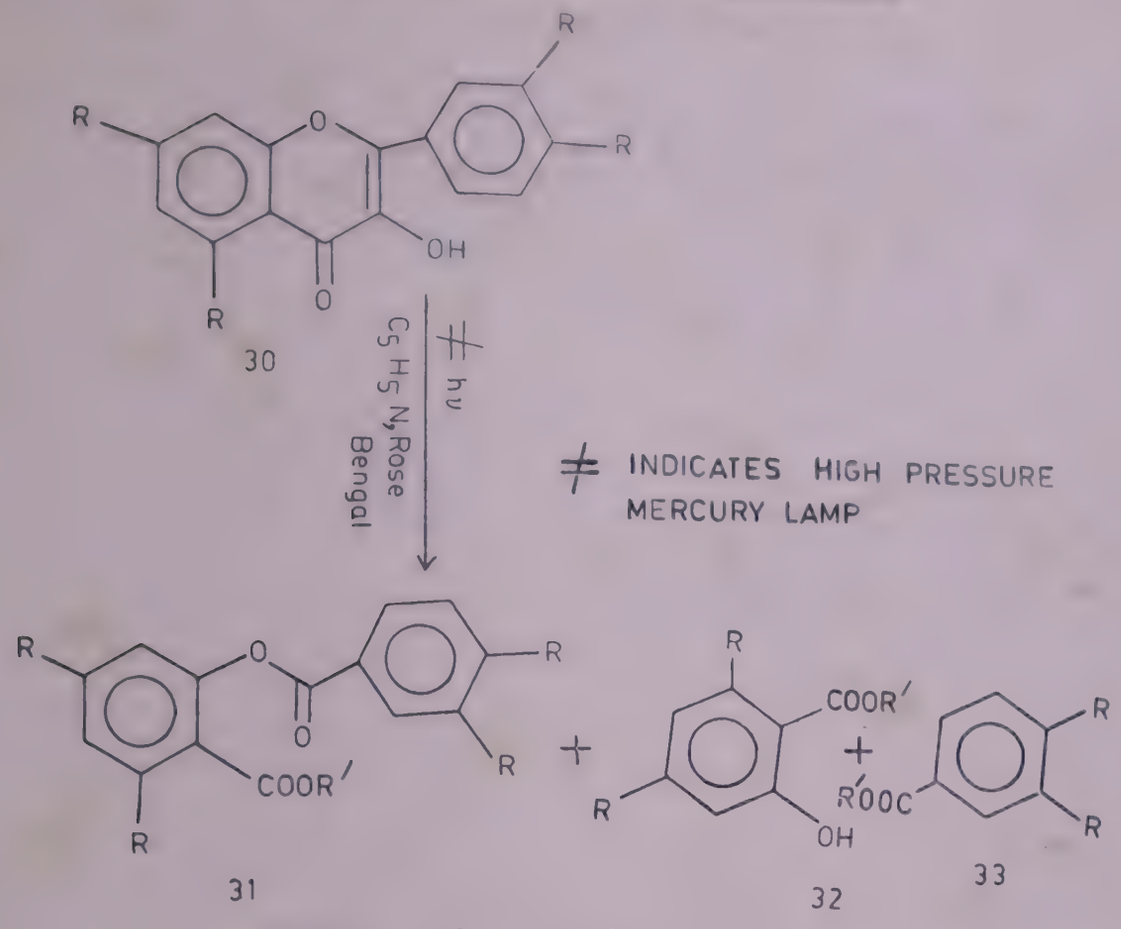


Photochemistry of Flavones, Flavonols and 3-Methoxyflavones

Hydroxy- and methoxyflavones, which are devoid of 3-oxygenation, seem to be highly stable towards light. On the other hand, flavonols and 3-methoxyflavones undergo a variety of changes in the presence of light with or without oxygen.

Kaneta and Sugiyama[50,51] carried out a qualitative study of the stability towards air and light of various naturally occurring flavones and flavonols which are used as dyestuffs either as such or in the form of complexed salts. Experiments with quercetin, morin, arthraxin, luteolin, 8-acetyl-5,7-dihydroxy-3′, 4′-dimethoxyflavone and tricin revealed that the hydroxylated heterocyclic ring attached to the flavone nucleus of arthraxin or present in flavonols, could be easily decomposed by irradiation. The complex salts of flavones, in contrast to those of flavonols, show high resistance to light even when air is buboled through their methanolic solutions.

Matsuura *et al.*[49,52] carried out irradiation of four flavonols (**24**a-**24**d) in isopropyl alcohol-benzene mixture in the presence of nitrogen. Each of them gave only one crystalline compound in 70-90% yield. The products were assigned the structures 1-hydroxy-1-phenyl-2,3-indandiones (**26**a-**26**d) respectively on the basis of their NMR, UV and IR spectral data. The formation of the indane derivatives (**26**) shows that flavonols undergo rearrangement upon irradiation with light. This rearrangement has been explained through the intermediacy of 2,3-epoxy-2-hydroxy-1-indanone intermediate (**25**) which may be formed by a formal ($\sigma^2+\pi^2$) cycloaddition reaction[53] analogous to the transformation of 2-cyclohexadienones into bicyclo[3 : 1 : 0]hex-3-en-2-ones (so-called lumiketones). The conversion of **25** into **26** may occur thermally, in the same way as that of an acetoxy-epoxide into an α-acetoxy ketone. The intermediacy of the epoxide (**25**) was supported by the isolation of the epoxide (**28**) and indanedione (**29**) from the



FOR 30: (a) R = OH, (b) R = OMe, (c) R=H

FOR 31-33: (a) R = OH, R′=H, (b) R=OMe, R′=Me
(c) R = H, R′= Me

photolysis products of 2,6-dimethyl-3-hydroxy-γ pyrone (**27**)[54]. It may be noted that quercetin (**24**e) resisted photolysis[49]. This is due to intramolecular quenching through the hydrogen bond between the 5-OH and 4-CO groups.

Flavonols undergo various oxidative degradations in the presence of light and oxygen. Matsuura *et al.*[55,56] irradiated three flavonols, viz. quercetin (**30**a), its 5,7,3′,4′-tetramethyl ether (**30**b) and 3-hydroxyflavone (**30**c) in pyridine in the presence of catalytic amount of Rose-Bengal. In all the three cases, the non-volatile product was found to be a mixture of a depside (**31**) and two carboxylic acids (**32**) and (**33**) originating from rings A and B; the volatile components were CO and CO_2.

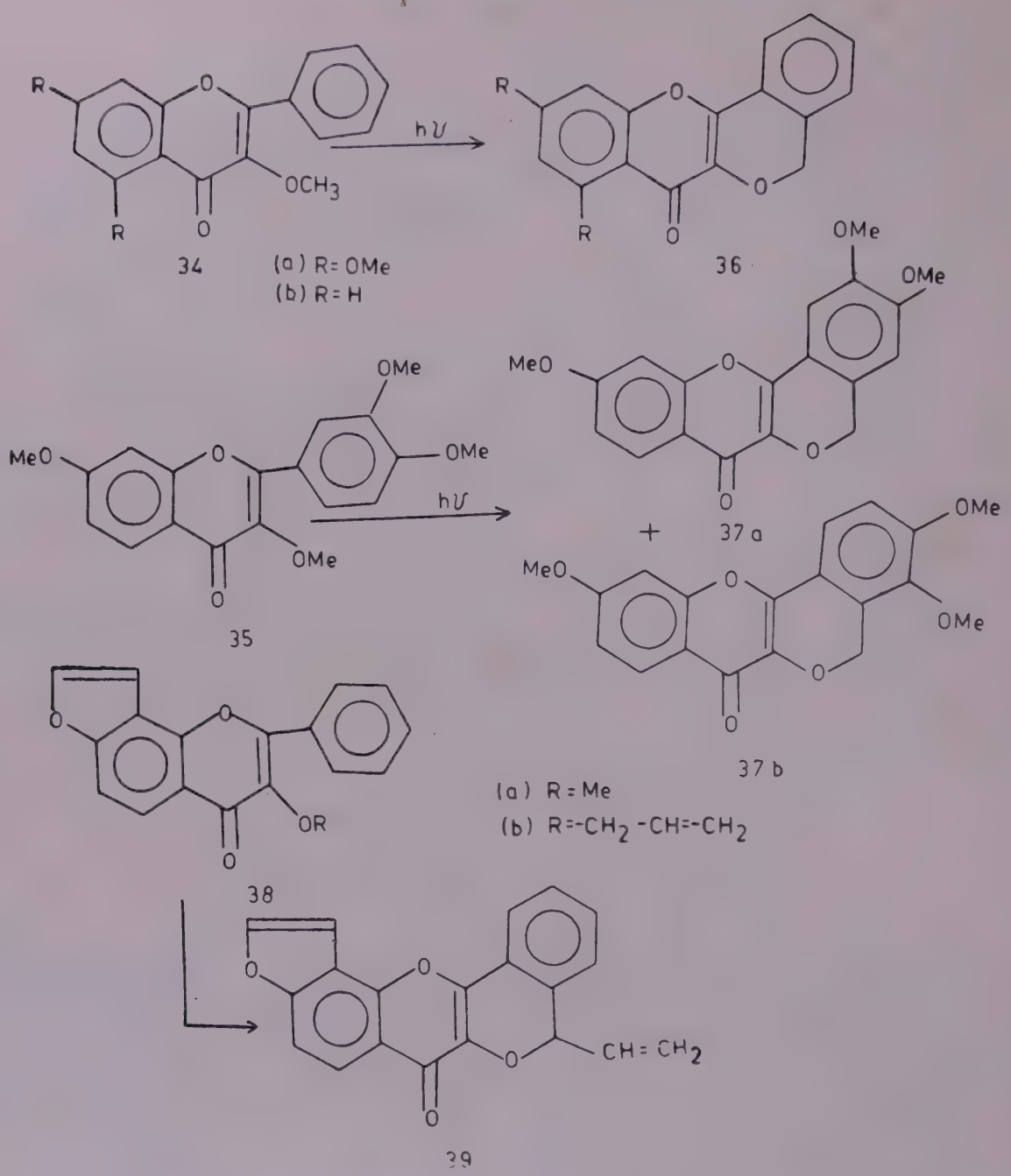
Photochemistry of 3-Methoxyflavones

3-Methyoxyflavones have been found to be sensitive to light both in the presence and absence of oxygen. Waiss *et al.*[57,58] studied quercetin pentamethyl ether under different conditions. When this compound was irradiated at 350 nm in methanol under nitrogen using a low pressure mercury lamp, four compounds were isolated. These were lumi-methyl quercetin (yield, 16%), α-photomethyl quercetin, β-photomethyl quercetin (yield, 31%) and 5-methoxy-β-photomethyl quercetin (yield, 1%). When irradiation was carried out in deoxygenated benzene, the photoreaction was observed to proceed at twice the rate compared to that in methanol solution and only α- and β-photomethyl quercetins were obtained.

Parallel photoreactions were carried out using galangin trimethyl ether (**34**a)[59] simple 3-methoxy flavone (**34**b)[49]; and 3,7,3′,4′-tetramethoxyflavone (**35**)[40]. In the first two cases, only one photoproduct — peltogynin derivative (**36**a and **36**b respectively) — was isolated. But in the case of **35**, a mixture of two peltogynins (**37**a and **37**b) was obtained; these were methyl ethers of naturally occurring peltogynin and mopanin respectively. In fact, the photoreaction with 3-methoxyflavones is so facile that Grambow *et al.*[59] cautioned that TLC analysis of 3-methoxyflavones should be carried out only in darkness.

The photochemical reaction of karanjin (**38**a), present in the seeds of *Pongamia glabra*[60], has been studied by Gupta and Mukerjee[61] under a variety of conditions. The main product, photokaranjin, was obtained from it in different yields, depending upon the solvent used. 3-O-Allyl-3-O-desmethyl karanjin (**38**b) prepared from karanjonol was also irradiated by the same workers[61] in tetrahydrofuran, when 5-vinylphotokaranjin (**39**) was obtained. Further, it may be emphasized that the furan ring remains unaffected during photoreaction.

Matsuura and Matsushima[62] irradiated 3-methoxyflavones under bubbling oxygen and got a mixture of photoproducts. For example, on irradiating 3,7-



dimethoxyflavone, a mixture of peltogynan (**40**, 4%) and its oxidation product—a lactonic compound (**41**, 11%)—was obtained.

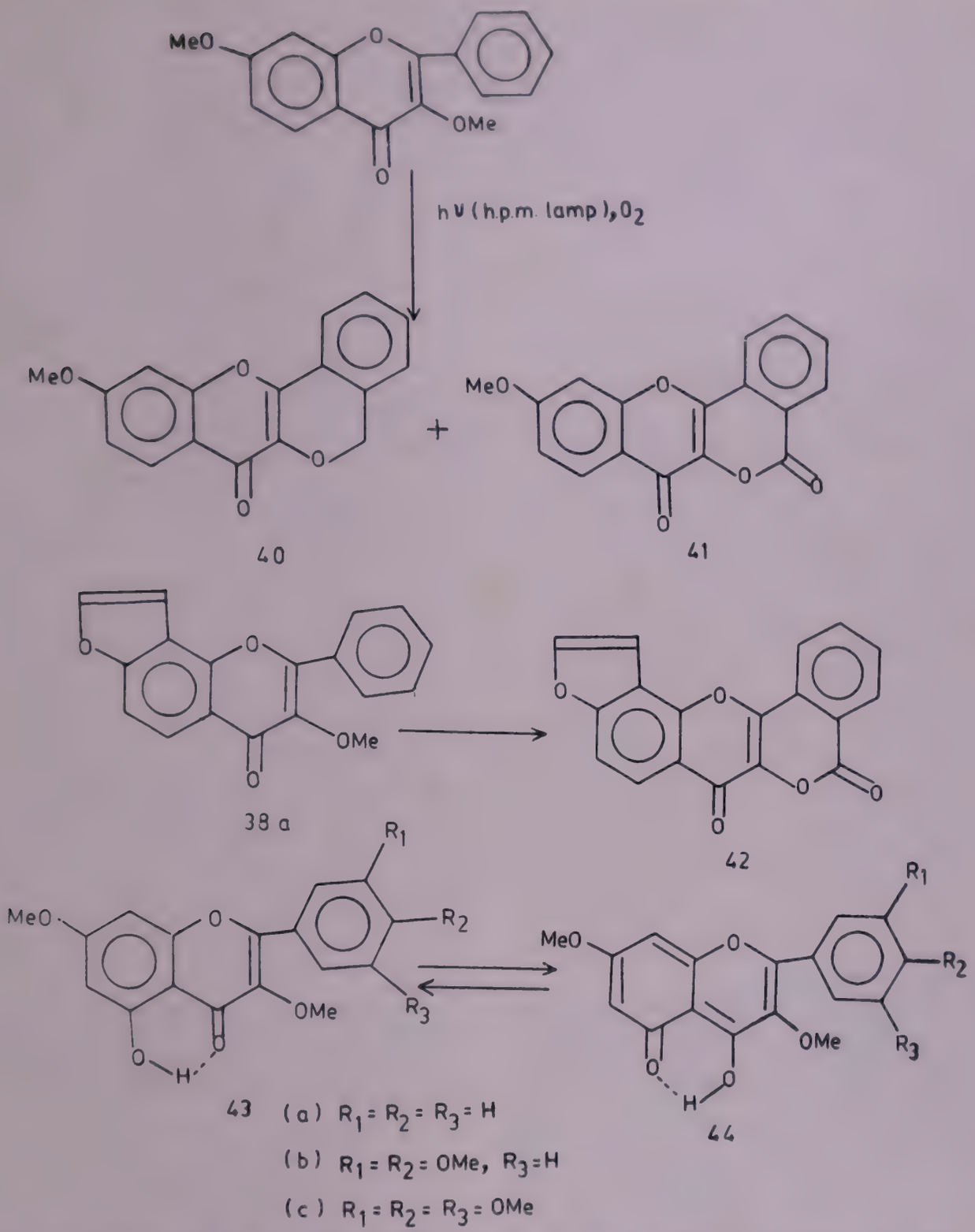
When 3-methoxyflavone was irradiated, two products, salicylic acid and a lactonic compound of the type **41** (11%), were obtained. But irradiation of karanjin (**38a**) for 4 hr gave only one photo-product[63]; it was shown to be a lactonic compound (**42**) on the basis of spectroscopic data.

It was further noted that 5-hydroxy-3-methoxy-flavones, such as 3,7-dimethoxy-5-hydroxyflavone[62] (**43a**), quercetin-3,7,3′,4′-tetramethyl ether (**43b**) and myricetin- 3,7,3′,4′,5′-pentamethyl ether (**43c**) did not undergo analogous photocyclization[62]. This stability towards photo-oxidation can be ascribed to the hydrogen bonding of the 5-hydroxyl group to the 4-carbonyl group and irradiation may promote only simple tautomerization to yield compounds of the type (**44**) which would resist further reaction.

Photochemistry of Isoflavonoids and 2,3-Diphenyl Chromones

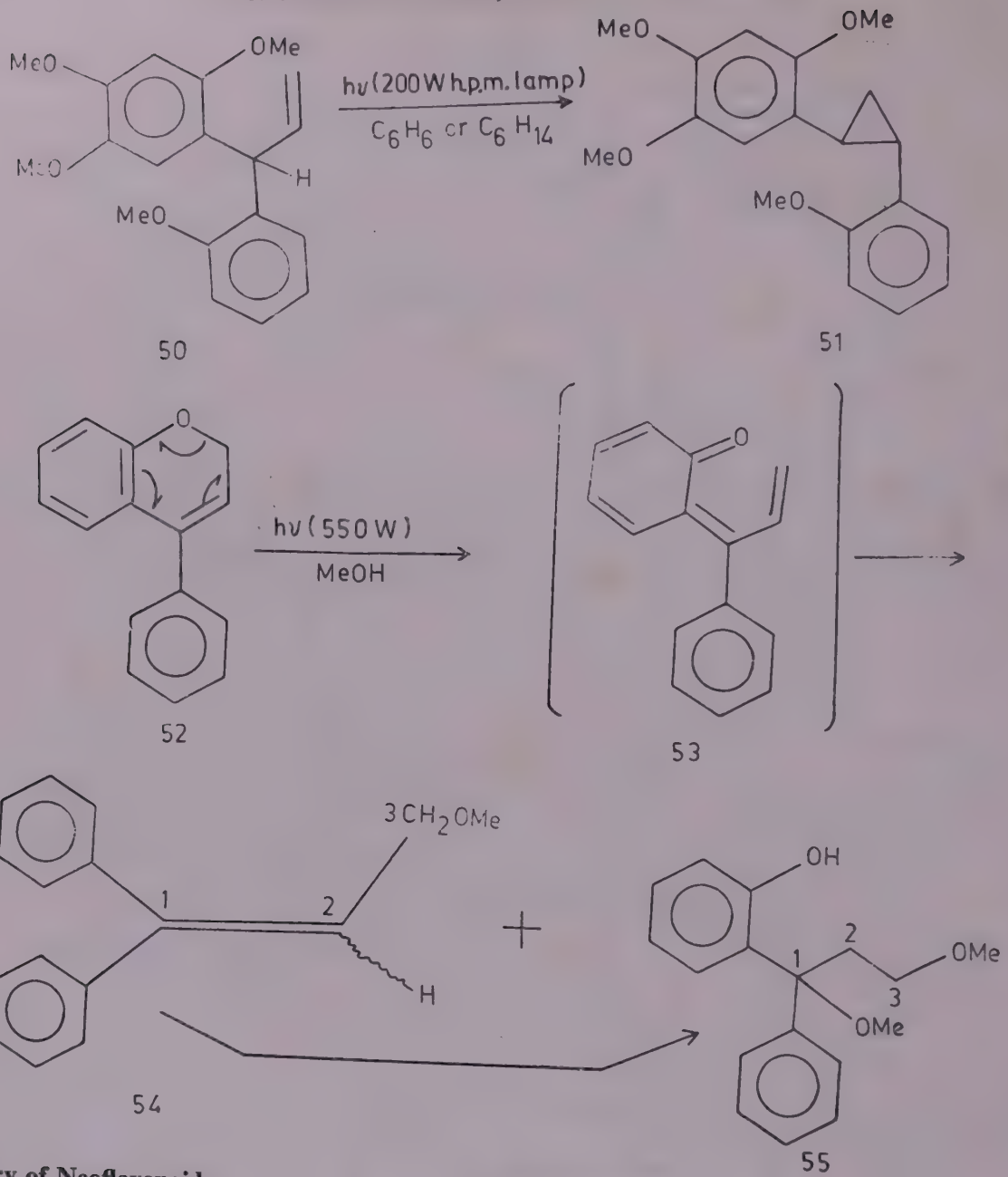
Isoflavones like 2-methyl- and 2-methyl-7-hydroxy-isoflavones, when irradiated with UV light, were recovered unchanged[64]. However, 2-phenylisoflavones (or 2,3-diphenyl chromones) are reactive and undergo rearrangement as well as oxidative coupling. Thus, irradiation of 2-phenyl-7-hydroxyisoflavone (**45a**) or 2-phenyl-7-methoxyisoflavone (**45b**) in methanol gave mainly two products in each case. These were: 3,4-diphenyl isocoumarin (yield, 10%) and a phenanthro-(9,10-c) isocoumarin derivative (**47a** or b) (yield, 42%). In the case of **45b**, a third compound was also isolated.

Since further irradiation of **46a** in methanol gave **47a**, it was concluded that **47** is derived from **46** by a photo-oxidative cyclization step[65]. The formation of **46** from **45** has been explained by steps of re-arrangement giving rise to an intermediate and



subsequent photochemical transformation. This is supported by photochemical valence tautomerization of 2,3-epoxyindanones to benzopyrylium-3-oxides followed by isomerization to isocoumarins[66,67].

A number of dehydrorotenoids (**48a-48d**) having differently substituted ring E were irradiated by Suginome *et al.*[68]. It was observed that if irradiation was done in the presence of sodium borohydride, lactonic compounds called rotenonones (**49a-49d**) were formed in different yields. On the other hand, irradiation in the absence of sodium borohydride produced no isolable compound. Rotenone and isorotenone remained unchanged under similar conditions, even in the presence of sodium borohydride. It is significant that various types of furan rings remain unaffected during the photochemical reaction. Recently, dehydrorotenones (**48a** and **48c**) were irradiated in the presence of oxygen by Chubachi and Hamada[69]. In the case of **48c**, two compounds were isolated; the major compound (25%) was rotenonone (**49c**) and the minor one (3%) was assigned the structure 1,2-dihydro-2-isopropenyl-8,9-dimethoxy-benzofurano-(2,3-b) furo(2,3 - h)benzypyran- 6 - one.



Photochemistry of Neoflavonoids

In the group of neoflavonoids, latifolin dimethyl ether (**50**) was the first to be subjected to irradiation[70] and the product obtained was an isomeric compound having 1,2-diaryl cyclopropane structure (**51**). Another neoflavonoid examined photochemically was the unsubstituted 4-phenyl-3-chromene (**52**). Its irradiation was carried out by Padwa *et al.*[71] in methanolic solution, when a mixture of three photoproducts was obtained. These were identified as *cis*- and *trans*-1-phenyl-1-(*o*-hydroxyphenyl) -3-methoxy-1-propenes (**54**) and 1-phenyl-1-(*o*-hydroxyphenyl)-1,3-dimethoxypropane (**55**). The compound **55** was shown to be a secondary photoproduct derived from **54** by further irradiation. The product (**54**) was accommodated in terms of 1,6-addition of methanol to the initially formed *o*-quinoneallide intermediate(**53**).

Summary

Recent developments in the chemistry of certain flavonoids, such as 2'-hydroxychalcones, chalcone epoxides, flavonoids, 3-methoxy-flavones, 2-phenylisoflavones; dehydrorotenoids and neoflavonoids are reviewed.

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REVIEWS

ELECTROMAGNETISM, ELECTRON THEORY AND SPECIAL THEORY OF RELATIVITY by A.K. Dutta (The Macmillan Co. Ltd, New Delhi), 1977. Pp. 331. Price Rs 20·00

Any new book on the general subject of electrodynamics suffers from the disadvantage of comparison with some excellent books already existing in the literature (e.g. Jackson's classical electrodynamics). Judged by such a yardstick, it is difficult to look at a new addition to the literature with anything but a critical eye. The book under review cannot be an exception to such a working hypothesis. The author has attempted to condense a vast scope, ranging from electromagnetism through electron theory and all the way to the special theory of relativity, within a comparatively small space of about 300 pages. This is a laudable effort by any standards, for why should it be necessary to elaborate on things, just for the fun of it, if it is possible to do justice to the chosen material within a smaller space? And it is with such an expectation that this reviewer started looking at the book. Unfortunately he was disappointed. The topics appear to be much too disjointed, the discussions much too abrupt, and a physical motivation much too lacking for even a casual reader to get the impression of an integrated approach to such an exciting subject. There are plenty of examples to show that while relatively elementary and conventional topics are developed with considerable care, detailing all steps, a corresponding degree of elaboration is lacking in some of the more advanced topics (despite greater need in the latter case). All in all, the book appears to be useful only in company with another standard treatise on the subject.

Yet there is one refreshing aspect in the book which deserves unreserved commendation, and this concerns the set of problems at the end of each chapter. These problems which are carefully framed, perhaps constitute the only concrete evidence of the author's known reputation as a good teacher. The student who uses the book will do well to attempt as many of these problems as he can on his own.

A.N. MITRA

OPTICS by Ajoy Ghatak (Tata McGraw-Hill Publishing Co. Ltd, New Delhi), 1977. Pp. xx + 538. Price Rs 31·50

The book under review is a welcome addition to the undergraduate textbooks on optics. The book is indeed touched with certain elegance. Both geometrical and physical optics have been presented in this single volume and naturally one does not expect to find everything on optics in this treatise. The book is divided into seven parts comprising twenty-two chapters. After introducing the readers to what is 'light', the author gets down to the discussion of the conventional geometrical optics in Part I. The application of matrix method in paraxial optics has given this book not only a distinguished appearance but the author has also shown the convenience of the method for tracing rays through complex optical systems. In Part II, vibrations and waves have been discussed in five chapters dealing with simple harmonic motion, forced vibrations, application of Fourier series, wave equation and Huygens' principle. In Chapter 4, the dependence of refractive index on wavelength has been discussed and that the long wavelength radiation is transmitted by ionosphere has been explained. The propagation and spreading of a wavepacket have been treated in Chapter 7 using Fourier integral theorem.

One of the best treated subjects is that of interference. Space has been allotted liberally to this topic and one complete part (III) of the book consisting of five chapters deals with interference. The subject is very well presented. Localization of interference fringes has been discussed at length. Making a full chapter on coherence is thoughtful. The concepts of spatial and temporal coherence have been developed. Discussion on optical beats and inclusion of the experiment of Lipsett and Mandel have brought the topic to an up-to-date level.

Part IV of the book deals with diffraction of light. In Chapter 15, in addition to Fraunhofer diffraction, topics of current interest like self-focussing phenomenon and spatial frequency filtering have also been discussed. A fairly rigorous treatment of Fresnel diffraction and analysis of transition from the Fresnel region to the Fraunhofer region have been made in Chapter 16. Holography is finding wide application these days. In the following chapter, the basic principle of holography and some of its applications have been presented in a lucid manner.

In Chapter 18, polarisation and double refraction of light and also production and analysis of polarised light have been discussed. Electromagnetic theory of light is the subject of the following two chapters. Maxwell's equations have been stated and the physical significance of the equations has been pointed out. The laws of reflection and refraction of plane electromagnetic waves by a plane dielectric and a plane metallic surface have been derived.

Photoelectric effect and Compton effect which establish the particle nature of light have been discussed in Chapter 21 in the conventional fashion.

In the last chapter, the basic physics of a laser has been discussed. The discussion here is concise and proper emphasis is maintained on He-Ne and ruby lasers; it may be read even by an undergraduate student with delight.

Inclusion of as many as nineteen beautiful plates adds to the value of the book. A comprehensive bibliography is appended to each chapter.

Inspite of all these novelties, this treatise may not be accepted as a textbook by many undergraduate students, as the syllabi of many universities in this country are not adequately covered. Students may be missing discussion on many traditional topics like optical instruments and vision, photometry

and velocity of light, colour photography and colour printing, etc. Spectroscopy has not been discussed at all. In the chapter on polarisation and double refraction one will be missing introduction to optical rotatory dispersion, particularly when ORD is being used as a useful tool for molecular configuration study. Though a large number of problems are given at the end of each chapter, inclusion of some worked out problems would have made an average student feel at ease.

To sum up, this book meets a need and the reviewer has mentioned what seemed to him omissions simply to draw the attention of the readers to subjects they may want to look elsewhere. This book should find wide demand.

T.N. MISRA

MICROBIOLOGY by Michael J. Pelczar (Jr), Roger D. Reid and E.C.S. Chan (Tata McGraw-Hill Publishing Co. Ltd, New Delhi), 1977, Pp. VII + 960. Price Rs 57·00

The fourth edition of this book does not differ much from the third, and those who liked the earlier version will like this one too. The book remains what it was, a good, unpretentious book for the beginner that is written in a straightforward and lucid manner. It is useful in the classroom, but admittedly it simply covers the usual familiar ground, without providing unexpected insights or bold new interpretations.

Chapter 3 ("Characterization and classification of Microorganisms") has been revised to correspond to the 8th Edition of Bergey's Manual and Chapter 11 ("Bacterial Metabolism") has been recast in a more logical order. Chapter 12 ("Modifications, Mutations and Genetics") and Chapter 19 ("Viruses") have been updated, reorganized, and rewritten. A new chapter on "Fundamentals of Microbial Ecology" has been added to Part Six as an introduction to the field of environmental and applied microbiology. Schemes of classification of microorganisms have been placed in Appendix A, where they are readily available for reference. Characteristics of selected genera of bacteria, algae, fungi and protozoa are arranged separately in Appendix B.

All introductory texts that take a "soup to nuts" approach are faced with a common problem, namely, how to be brief and simple, and yet remain technically correct. Mostly the authors succeed, but occasionally they are so brief as to be cryptic. Thus, in discussing the respiratory chain (p. 175), they observe that NAD, FAD and coenzyme Q can exist in reduced and oxidized forms, but then do not go on to reveal how their structures account for these two forms.

On the balance the authors have succeeded in their purpose and have given us a compact, readable overview of the field for the introductory university course. The availability of a relatively inexpensive Indian edition will undoubtedly help its acquisition by the colleges in this country.

T. RAMAKRISHNAN

EUCARYOTIC MICROBES AS MODEL DEVELOPMENTAL SYSTEM : MICROBIOLOGY SERIES, Vol. 2, edited by Danton HO' Day and Paul A. Horgen (Marcel Dekker Inc., New York), 1977. Pp. xiv + 440. Price $ 39·75

Since unraveling the genetic code and assigning the base triplets which determine, in turn, the amino acid sequence in the synthesis of specific proteins, the most important question that is yet to be understood is the problem of 'differentiation'. This is no new question, since from the early days of embryological studies, biologists have made efforts to understand the phenomenon. It is known that in every sexually reproducing eukaryotic organism (even in the case of parthenogenesis) the fertilized egg develops into an adult by a highly regulated and time-bound programme and any disturbance caused to this precise process leads to abnormalities and even death of the embryo. With the advent of developmental genetics it was shown that lethal mutations can cause developmental abnormalities leading to the malformation or even death of the embryos, indicating very clearly that regulation of developmental processes is a function of gene expression in time and space of growth. In as much as the present day concepts have linked the DNA as the information molecule, all developmental processes should have an imprint in its base composition and sequence. Thus, an orderly progress such as development and differentiation must be the result of a very precisely controlled expression of genes and the mechanism that controls this expression is in reality what differentiation is.

In understanding this process of differentiation at molecular level, many systems have been used. Invariably systems, such as tissue culture, cell hybridization, etc., involve cells derived from higher organisms and they are not always suitable for analysis due to great genetic complexity. There have been efforts to look for simpler systems to understand the fundamental aspects of differentiation. In this regard, some of the protozoans, slime molds, offer investigators a very vast area for research. The life histories of these organisms are simple and culturing techniques are not very demanding. It is rather surprising that not many developmental biologists have used these systems for research. The present compilation is very timely in this context.

The book is divided into three parts: (a) Growth and cellular differentiation; (b) Cell communication and morphogenesis; and (c) Dormancy and germination. Each section is introduced by an editorial comment in regard to the scope of the articles in that section. For those who are desirous of using these primitive yet interesting organisms, the first section is very useful, as life histories and points of interest of study in each case have been given. Most of the articles included in the book bring to focus some aspects of differentiation at molecular level. Thus, it is a very useful reference book for all cell and developmental biologists.

C.M.S. DASS

Notes & News

Molecular hydrogen detected in galaxy outside our own

Although hydrogen in its atomic form is well known, molecular hydrogen was not observed until 1970 in our Milky Way galaxy. Dr Rodger I. Thompson, Marica Lebofsky, and George Rieke, at the University of Arizona in Tucson have detected molecular hydrogen in a galaxy 60 million light years from Earth and have confirmed the existence of large amounts of cosmic dust thought to be the source of enormous amounts of infrared radiation coming from that galaxy (*Astrophys. J. Lett.*, June 1, 1978). The researchers observed molecular hydrogen in the galaxy designated NGC 1068, one of the most famous of a group called Seyfert galaxies.

Besides being the first observation of this basic molecule in any place except our own galaxy, the detection of molecular hydrogen in NGC 1068 provides new information about the galaxy itself. For molecular hydrogen to exist, it must reside inside a cosmic dust cloud which protects it from starlight that will break it up into two atoms. Therefore, the detection of molecular hydrogen also confirms the existence of great amounts of dust.

Observation of the molecule also requires that it be excited by shock waves which indicate the existence of violent events, such as explosions, in the centre of the galaxy. The molecules must be in this excited state to send the infrared signals detected by the Arizona team. In our own galaxy molecular hydrogen is often associated with the regions where new stars are being created: therefore, new stars may be created in NGC 1068.

Molecular hydrogen has been difficult to find because it gives off energy predominantly in the infrared part of the electromagnetic spectrum where the usual optical and radio telescopes do not operate. The University of Arizona team used very sensitive equipment which was specially designed for infrared work at the university's 90-in Steward Observatory telescope.

This observation may represent an advance in the science of infrared astronomical spectroscopy which should open the way to many new discoveries in the infrared properties of distant galaxies.

Zeeman effect absorption spectrometry

T. Hadeishi of Lawrence Berkeley Laboratory, California, USA has reported a new application of Zeeman effect—splitting of a spectral line in a magnetic field—for simple and accurate atomic absorption spectrometry (termed ZAA) in the analysis of trace elements in commercial samples. The idea to use Zeeman effect came from the need for rapid assessment of mercury contamination in fresh fish catches in Japan. The ZAA technique not only eliminates the need for complicated double beam optics of the conventional atomic spectrometers, but it also has efficient performance and enhanced tolerance against background noise factors, due, for instance, from impurities in samples from background interference. Thus, ZAA does not require elaborate pretreatment and sample preparation.

Two commercial types of Zeeman effect absorption spectrometers have been developed by Hitachi Ltd (Japan) and its U.S. subsidiary, Nissei Sanyyo Instruments, California respectively. In type I ZAA, the magnetic field is applied to the sample chamber, while in type II the field is applied to the light source. In the Zeeman effect, the magnetic field H splits the input monochromatic light into three polarized components ($\sigma\pm$ and π). The π–component is just the input light wavelength accounting for half the input intensity and is plane polarized in a plane parallel to the magnetic field while the fainter circularly polarized σ_+- and σ_--components are slightly frequency shifted respectively above and below the input light frequency. In ZAA, the π- component light frequency is matched with a particular absorption frequency of the trace element in the sample to be analyzed, so that the π-component is effectively absorbed and the σ-components pass through and are monitored.

In type I ZAA, the input light beam, with the aid of a rotating polarizer, is alternately polarized in planes parallel and perpendicular to the magnetic field (H) of a solenoid. The solenoid surrounds a graphite cuvette electric furnace in which the sample to be analyzed is located and heated. As explained earlier, the trace element in the sample allows the σ-component lines only to pass through. An electronic detector measures the intensity of these lines in relation to the input intensity from which the absorption parameters and concentrations of the trace elements are determined.

In type II ZAA, the magnetic field is applied to the source instead of the sample chamber. A rotating polarizer allows $\sigma\pm$ - and π -components to pass alternately through the vapourized sample. As before, the π- component is absorbed and also diminished by scattering, whereas the σ-components practically pass through with negligible scattering, and are then monitored electronically.

The performance of both types of ZAA spectrometers is similar, but type I is beset with the difficulty that magnetic field is applied in a high temperature medium of graphite furnace; this restricts the sample size to within a few milligrams only. However, type I ZAA does not have the limitation of type II instrument in the need for a special type of light source (viz. magnetically-confined lamps) for operation in intense magnetic fields. ZAA devices may find diverse applications, such as analysis of trace elements in sea water, ceramics, geology, shale-oil, and in blood and urine samples [*Science*, **198** (1977), 39].

New gamma signal could be nearby neutron star

Evidence for the existence of a γ-ray source with the unusual period of 59s, which is increasing, suggests to Cambridge astrono-

mers that there may be a neutron star orbiting a visible star only 30 par sec away [*Nature, Lond.*, **271** (1978), 634].

Researchers came across data on the γ-ray source [referenced as {CG 195+4 (Geminga)}] collected by the COSB and SAS2 satellites. It was found to be interesting, because no other sources of γ-rays with periods in this range are known. Several pulsars send out γ-rays with periods of less than 1s (gradually increasing) and periodic X-ray sources fall into two groups with periods less than 10s and over 200s.

The source was assumed to be an ordinary visible star with a neutron star companion. This idea is based on theoretical studies of the evolution of binary systems that include a neutron star. This suggests that before the neutron star starts to accrete matter and spin up emitting X-rays in the process, it goes through a stage in which it is spun down in the weak stellar wind of its companion. The gradual lengthening of the γ-ray periods suggests that the neutron star responsible is in the latter phase.

From the nature and direction of the γ-ray flux, and the theory of neutron star binaries, enough information was derived to pick out likely visible companions from the star maps and γ-Geminorum, an early type star was hit upon.

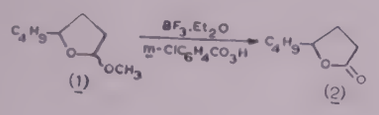
It is suggested that γ-rays are produced through the interaction between the gas of non-accreted matter that surrounds the neutron star and its strong magnetic field. This results in gas being thrown away from the neutron star. A fraction of the energy released in this interaction (estimated at 0·17) is in the form of electrons moving very close to the speed of light.

About half of these will lose energy by radiating UV photons, which in turn can pick up more energy from the remaining energetic electrons. It is this mechanism that is responsible for the observed γ-ray pulses.

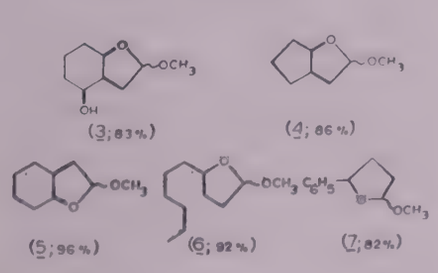
The frequency of the pulses of the γ-flux is in a range previously unobserved, probably because such signals could not now be observed unless they came from a near source, and its detection poses a challenge for future γ-ray observations [*New Scient.*, **77** (1978), 503].

One-step conversion of lactols into lactones

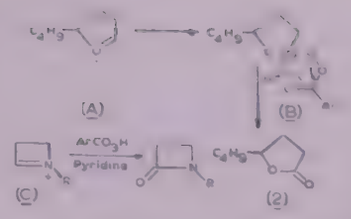
A method for direct one-step conversion of protected lactols to lactones has been reported from Department of Chemistry, University of Pittsburgh. The method involves treatments of the protected lactol with 1·1 equivalent of *m*-chloroperbenzoic acid in methylene chloride containing a catalytic amount of boron trifluoride etherate. Yields for the conversion of protected γ-lactols to γ-lactones are generally high. As a typical example, the conversion of the cyclic methyl acetal (1) into γ-octanoic lactone (**2**) takes place as follows:



A solution of protected γ-lactol in 3·6 ml of dry methylene chloride containing a catalytic amount of boron trifluoride etherate was treated at room temperature with *m*-chloroperbenzoic acid. After 3 hr, the reaction mixture was diluted with 30 ml of ether and washed with 10% aqueous sodium thiosulphate, saturated sodium bicarbonate, and brine. The crude product obtained after drying ($MgSO_4$) was chromatographed on 20 g of silica gel using hexane-ether (1:1) giving 133 mg of pure lactone (**2**) as a colourless oil. Application of this method to protected δ-lactols gave rather low yields of δ-lactones.



The above reaction proceeds via oxonium (*A*) which reacts with peracid giving rise to intermediate (*B*). Rapid fragmentation of (*B*) leads to the observed lactone in the absence of base.



A similar reaction in which the iminium salt (*C*) generated from azetidine-2-carboxylic acid is reacted with *m*-chloroperbenzoic acid in the presence of pyridine to form β-lactams has been reported [*Tetrahedron Lett.*, (1978), 419].

International Journal of Applied Analysis (IJAA)

This new six monthly journal started in 1977 by the Department of Mechanical Engineering, University of California Berkely, will publish articles devoted to the critical mathematical analysis of the problems concerning management science, operations research and topics of current interest in applied and abstract sciences. Analysis of problems of interdisciplinary character will be given special coverage. Authors of accepted paper will have to pay Rs 40 or $ 10.00 per printed page. Further details regarding the journal can be had from Dr Sudhanshu K. Ghoshal, Department of Mechanical Engineering, University of California, Berkeley, California 94720, U.S.A. In India, these can be had from Dr P.C. Bhakta, Department of Mathematics, Jadavpur University, Calcutta 700 032. The annual (for 12 issues) subscription rate for the journal is Rs 50 or $ 16·00.

Structural Engineering Research Centre, Roorkee/Madras

According to the annual report of the centre for 1976-77, it undertook 28 research projects and 14 consultancy projects during the year. The surveys of live loads on the New Yamuna Bridges at Agra and the Hindon Bridge at Ghaziabad were completed and a report containing recommendations on design live loads for bridges was prepared. The know-how for the production of small capacity grain storage bins in ferrocement was released to a party through the National Research Development Corporation of India. Work was

also continued on the design of biogas plants for both individual and community use. The other projects in progress at the Roorkee Centre include interaction analysis of prestress losses, computer analysis of guyed towers, and automated dynamics analysis of three-dimensional rigid-jointed towers and frames. Work on the preparation of an explanatory handbook for the Code of Practice for Structural Concrete was continued at the Roorkee Centre.

The method of evaluation of prestress losses developed earlier was modified so as to take into account the actual locations of the individual rows of tensioned and untensioned reinforcement. The method also takes care of the variation of the modulus of elasticity of concrete with time and also the variation of the superimposed dead loads applied, if any, at any time interval. A general computer programme has been developed for the estimation of prestress losses in pretensioned beams with or without untensioned reinforcement.

Software was developed for finding the natural frequencies and modes of plates for any type of boundary conditions using triangular plate elements. It is now possible to assess the natural frequencies and determine the mode shapes for simple or T-beam floor grids, multi-girder or beam-slab bridge decks, and plates of different shapes under different boundary conditions.

Another important project related to the development of small-capacity ferrocement bins useful to rural farmers. A semi-mechanized casting process was developed for casting ferrocement cylindrical wall units. The dimensions of the various prefabricated components of the ferrocement bins were standardized in such a manner that the weight of any single component did not exceed 120 kg. These bins can be assembled easily with manual labour (4 to 5 persons).

Analysis and design of cylindrical ferrocement bins of up to 3 tonnes capacity using the classical theory of shells was carried out. Tests for waterproofing of the bin units were also carried out, and based on the tests, two coats of bituminous aluminium paint on the outer surface were recommended for above-ground bins. For underground bins, two coats of coaltar emulsion or bituminous paint were recommended. Load testing was done with grain on a 3-tonne unit. The behaviour of the bin was quite satisfactory under loading and unloading operations. Evaluation tests carried out at the Central Food Technological Research Institute, Mysore, showed that both the above-ground and underground bins were suitable for storage of food grains. A patent has been filed on this process.

In addition to grain storage bins the technology developed by SERC can be used for the manufacture of small capacity water tanks for household and farm use, especially to meet the demands for protected water supply in rural areas.

Work on the setting up of the model analysis laboratory at Madras is nearing completion. A photoelastic oven has been commissioned, and a 5-tonne universal testing machine is being installed. The following facilities were also established: Shadow moire and Lightenberg; Optical bench elements; Loading frame for holographic interferometry; and Reproduction of gratings. Tests in holographic interferometry included calibration and determination of the efficiency of holographic plates and discs under diametrical load and a cylindrical shell under point load. In the moire technique, a ribbed slab was tested using the shadow moire and Lightenberg techniques. Filtering and fringe sharpening experiments were conducted using the optical bench on a model of a wall panel under concentrated load. Three-dimensional photoelastic experiments were conducted on a cylindrical specimen under concentrated load using stress freezing technique. Many of these experiments were conducted during September-December 1976 under the guidance of Prof. C.A. Sciammarella, UN consultant on model investigations. It is proposed to develop suitable computer programmes for obtaining the final results from experimental data. The tele-terminal equipment has been installed and will be linked to the IBM 370/155 computer system available at the Indian Institute of Technology, Madras, as soon as the interface equipment is received. The Madras Centre made substantial progress in the installation of the tele-terminal and in the strengthening of laboratories for model analysis, polymer concrete, and structural dynamics and machine foundations, with UNDP assistance.

One of the important consultancy projects completed during the year relates to the investigations on the large diameter prestressed concrete pipes of Veeranam Water Supply Project. The know-how for the production of prestressed concrete sleepers for the Indian Railways has been released to a party. Several agencies are building ferrocement water tanks based on the designs furnished by the centre. The construction of the 144 residential flats by the Tamil Nadu Housing Board at Madras based on the on-site prefabrication system developed by SERC has been completed.

SERC continued to participate in the Karimnagar project. Besides providing detailed design and technical assistance in the construction of several buildings based on the know-how developed at the centre, it also helped in the setting up of a community gobar gas plant in a village in this district.

Physical Research Laboratory, Ahmedabad

The report of the laboratory for 1976-77 outlines its current as well as the proposed research and development activities. The work of the laboratory covers the following major areas: (i) solar and planetary physics, especially aeronomy and radio astronomy, (ii) infrared astronomy, (iii) plasma physics and laboratory astrophysics, (iv) theoretical physics, (v) nuclear, geo and cosmo physics, and (vi) archaeology and hydrology.

The main research projects of the Solar and Planetary Physics group during 1976-77 are: ground

and rocket-based, and ATS-6 geostationary satellite - based study (flares, solar winds, etc.) of the sun; interplanetary medium; earth's magnetosphere; ionosphere (sudden and travelling disturbances) and geomagnetism. ATS-6 satellite study of the equatorial ionosphere at Ooty in collaboration with the National Oceanic and Atmospheric Administration, USA revealed severe ionospheric radio scintillations (exceeding 15 dB) in hf, vhf and uhf bands at the equator. The plasmaspheric electron content over India has been found to increase during daytime and decrease during night. As a result of this, during night there is a downward flux of ionization from the plasmasphere which helps to maintain the nighttime ionosphere.

The laboratory has fabricated instruments for mapping ionospheric electron content and scintillations over an extended region, new rocket payloads, such as Rb magnetometer, photometer monitors for atmospheric ozone and molecular oxygen, thermal particle detectors and quadrupole mass spectrometers for ionosphere and sophisticated ground tracking and recording equipment for vapour release experiments. In particular, observations at Mt. Abu of OH night airglow have shown that internal gravity waves may be responsible for some fluctuations in the neutral temperature at 90 km. Further, the occurrence of varying electric fields in the dynamo region of the ionosphere may be due to wind fields and shears generated by gravity waves.

In the Plasma Physics Section, the following theoretical studies were conducted: plasma turbulence and solitonic solutions, Kelvin-Helmholtz instabilities and methods for their suppression, plasma heating, magnetosonic waves, etc. On the experimental side, laboratory simulation of space plasmas, production and confinement of high temperature plasmas, injection and trapping of electrons in magnetic mirrors, the effect of magnetic field on the interaction of plasma streams with neutral gases, etc. have been investigated. An experiment on the turbulent energy transfer between a high intensity electron beam and high density mirror confined plasma has been conducted. The Radio Astronomy Section measured infrared fluxes of stellar sources in the 1-2, 1-65 and 2·2 μ regions for the first time. For this purpose, the PRL stellar PbS photometric device, coupled to Nainital and Kavaloor radiotelescopes, was used. UV continuum sources, Seya-Namioka-type UV monochromator for generating narrow monochromatic photon beams (wavelengths 300-3000 Å with 0·6 Å width), photoabsorption chamber for studying photoabsorption cross-sections, etc. are some of the sophisticated instruments developed during the year.

The Theoretical Physics Group studied the astrophysical problems such as dynamics of spiral asteroids, planets, galaxies, etc. Kirkwood gaps, motion of plasmas around condensed matter, such as neutron stars and black holes, dynamics of accretion disc models for X-ray source. In the field of nuclear physics, the applications of self-consistent field theory and group theory for the ground and low excited states of nuclei have been investigated. Spectroscopic calculations for ground state of ^{8}Be, ^{12}C and ^{20}Ne using density dependent forces have been completed. Another significant achievement is the deformed configuration mixing shell model and its utility in the *fp*-shell nuclear spectroscopy. Some other topics of study include statistical spectral distribution theory, nuclear symmetries based on group theoretical concepts, atomic collision processes, photoionization in molecules, angular distribution functions of heavy hydrogen, etc.

In the field of geophysics and geocosmophysics, an understanding of the physical and chemical processes within earth and its cosmic environment has been achieved through a study of naturally occurring systems, such as meteorites and lunar rocks. The work is being done in collaboration with agencies like NASA, USSR Academy of Sciences and GEOSECS (Geochemical Ocean Section Studies). In particular, study of stone meteorite (classified as unequilibrated chondrites) that fell (Jan. 1976) near Dhajala (Surendranagar District, Gujarat) revealed that the meteorite had a preatmospheric radius of about 35 cm and had been exposed to cosmic radiation effects for nearly 7 million years. A study of solar flare tracks due to heavy nuclei in solar cosmic rays and microcraters due to bombardment of energetic cosmic dust grains in lunar samples and primitive meteorites has revealed that the energy spectrum is practically constant over the last 4 billion years. Further, it has been found that the flux of interplanetary micron size dust grains before this period ought to be much higher (about 5 times) than its present value. A method for determining solar flare exposure ages of lunar rock surfaces (Apollo samples) based on ^{26}Al isotope has been developed. From a systematic study of the chemical dynamics in the river-ocean interfaces (estuaries) of Narmada, Tapti and Godavari basins, the extent of mixing of fresh water with sea water in the transition region can be determined. This is achieved through the analytical determination of dissolved uranium and silicon concentration as a function of chlorosity. It has been found that while uranium isotopes are conserved in passing from river to the sea, silicon content is not always conserved, indicating biological factors responsible for nonconservation of silicon. Other studies comprise measurement of cosmogenic ^{10}Be in deep sea sediments, ^{20}Si and particulate matter in oceanic waters, especially the Atlantic ocean, for elucidating mixing patterns. Deposition of calcium carbonate and variation of rate of deposition were measured in the equatorial Pacific ocean. Scanning electron microscope study of millolites from Saurashtra coast confirmed that these deposits must have been formed through aeolian processes only.

In the field of Archaeology, ^{14}C dating studies of the ancient copper mining area of Rajpura Dariba (Udaipur District) pushed back the date of this mining area

beyond the first millennium B.C. Another mine near Jodhpur area has been dated to *c.* 2200 B.C. and the oldest date, *c.* 6300 B.C. has been obtained from Koldihawa (Allahabad District). Significantly, scanning electron micrographs of soil samples from ochre coloured pottery bearing archaeological sites in Western Uttar Pradesh revealed that these deposits might have been laid by flash floods and not by aeolian activity as believed earlier.

In the field of hydrology, the laboratory established (through measurement of uranium isotopes and dissolved SiO_2 in river streams and adjacent unconfined aquifers) that the Sabarmati river is effluent in the Ransipur-Sadra region with groundwater discharge during 1975-76 being 1% of the average inflow (20 million m^3) at Dharoi. Also, the principal cause of salinity increase in the coastal aquifers of this region is due to the ingress of sea water resulting from over-exploitation of aquifers. The effect of Dharoi Dam on these aquifers has also been studied.

Announcements

● *The* 1979 *Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy* will be held in Cleveland, Ohio during 5-9 March 1979. Symposia on the following topics are being organized during the conference. : (i) Liquid chromatography for environmental regulatory requirements; (ii) practical applications of glass capillary columns in gas chromatography; (iii) problems and solutions in capillary gas chromatography; (iv) ion chromatography; (v) photoacoustic spectroscopy; (vi) laboratory systems management; (vii) microcomputers/microprocessors and process control automation; (viii) new surface analysis techniques; (ix) trace analysis in characterization of materials; (x) environmental analysis of water and sediment; (xi) inductively coupled plasma emission; (xii) biomedical aspects; (xiii) new analytical techniques on the horizon; (xiv) 1979 awards symposium, (Spectroscopy Society of Pittsburgh, Society for Analytical Chemists of Pittsburgh, Hasler Award, Dal Nogare Award); (xv) Fourier transform/computer dispersive groups symposium; (xvi) ASTM E-42 — new surface analysis instrumentation; and (xvii) ASTM E-31—computerized laboratory systems; (xviii) Coblentz award symposium.

Papers in all disciplines (not restricted to the symposia topcs) of analytical chemistry and applied spectroscopy can be contributed. Workers interested in presenting papers in the conference may send a 300 word abstract in triplicate to Mrs Linda Briggs, 1979 Pittsburgh Conference, 437. Donald Road, Pittsburgh, P.A. USA 15235 by 29 August 1978. Further information regarding the conference can be had from Mr Allen J. Sharkins, Exposition Chairman, 1979 Pittsburgh Conference P.O. Box 2128, Lower Bussell P.A. 15068, U.S.A.

● *A Research & Industry Get-Together* is being organized by the Central Electrochemical Research Institute (CECRI), Karaikudi during 18-21 September 1978, as a part of the silver jubilee celebrations of the institute.

Major areas of discussion during the get-together will be: (i) Industrial electrolytic cells for production of organic and inorganic products; (ii) Electrometallurgy and electrothermal products; (iii) Electrodeposition and metal finishing; (iv) Corrosion and its prevention; (v) Power sources; (vi) Solid state electrochemistry; and (vii) Promotion of small scale and cottage industries in rural areas.

Further information regarding the get-together can be had from Shri V. Aravamuthan, Deputy Director, Central Electrochemical Research Institute Karaikudi 623 006.

● *The Society of Biological Chemists, (India)* is organizing the following symposia at Delhi University at the time of its annual meeting during 3-5 October 1978: (1) Symposium on agriculture and food biochemistry (3 October); (2) Symposium on nutritional and clinical biochemistry (4 October); and (3) Symposium on separation methods in biochemistry (5 October).

● *The Indian Institute of Chemical Engineers* invites nominations from corporate members of the Institute for the following annual awards, to be awarded at the annual session of the Institute: (1) Sir Shriram National Award of about Rs 9000 for leadership in Chemical Industry; (2) Hindustan Lever Award of Rs 4500 (approx) for the most outstanding chemical engineer of the year; (3) Indian Explosive Ltd Award of Rs 4500 for excellence in process/product development; (4) Herdillia Award of Rs 4500 for excellence in basic research in chemical engineering; (5) NOCIL Award of Rs 4500 for excellence in design/development of process plant and equipment; (6) Amar Dye-Chem Award of Rs 2250 for excellence in R&D for chemical engineers below 35 years.

Nominations may be sent by 31 August 1978 to the Honorary Secretary, Indian Institute of Chemical Engineers, Raja Subodh Mullick Road, Post Box No. 17001, Calcutta 700 032.

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